Queensland University of Technology

Discipline of Physics

Investigation of the effect of organics on the water uptake of marine aerosols

A THESIS SUBMITTED BY ROBIN LEWIS MODINI TO THE DISCIPLINE
OF PHYSICS, QUEENSLAND UNIVERSITY OF TECHNOLOGY, IN
PARTIAL FULFILMEMT OF THE REQUIREMENTS OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

June 2010

Abstract

Water uptake refers to the ability of atmospheric particles to take up water vapour from the surrounding atmosphere. This is an important property that affects particle size and phase and therefore influences many characteristics of aerosols relevant to air quality and climate. However, the water uptake properties of many important atmospheric aerosol systems, including those related to the oceans, are still not fully understood. Therefore, the primary aim of this PhD research program was to investigate the water uptake properties of marine aerosols. In particular, the effect of organics on marine aerosol water uptake was investigated. Field campaigns were conducted at remote coastal sites on the east coast of Australia (Agnes Water; March-April 2007) and west coast of Ireland (Mace Head; June 2007), and laboratory measurements were performed on bubble-generated sea spray aerosols. A combined Volatility-Hygroscopicity-Tandem Differential Mobility Analyser (VH-TDMA) was employed in all experiments. This system probes the changes in the hygroscopic properties of nanoparticles as volatile organic components are progressively evaporated. It also allows particle composition to be inferred from combined volatility-hygroscopicity measurements.

Frequent new particle formation and growth events were observed during the Agnes Water campaign. The VH-TDMA was used to investigate freshly nucleated particles (17-22.5 nm) and it was found that the condensation of sulphate and/or organic vapours was responsible for driving particle growth during the events. Aitken mode particles (~40 nm) were also measured with the VH-TDMA. In 3 out of 18 VH-TDMA scans evaporation of a volatile, organic component caused a very large increase in hygroscopicity that could only be explained by an increase in the absolute water uptake of the particle residuals, and not merely an increase in their relative hygroscopicity. This indicated the presence of organic components that were suppressing the hygroscopic growth of mixed particles on the timescale of humidification in the VH-TDMA (6.5 secs). It was suggested that the suppression of water uptake was caused by either a reduced rate of hygroscopic growth due to the presence of organic films, or organic-inorganic interactions in solution droplets that had a negative effect on hygroscopicity.

Mixed organic-inorganic particles were rarely observed by the VH-TDMA during the summer campaign conducted at Mace Head. The majority of particles below 100 nm in clean, marine air appeared to be sulphates neutralised to varying degrees by ammonia. On one unique day, 26 June 2007, particularly large concentrations of sulphate aerosol were observed and identified as volcanic emissions from Iceland. The degree of neutralisation of the sulphate aerosol by ammonia was calculated by the VH-TDMA and found to compare well with the same quantity measured by an aerosol mass spectrometer. This was an important verification of the VH-TMDA's ability to identify ammoniated sulphate aerosols based on the simultaneous measurement of aerosol volatility and hygroscopicity.

A series of measurements were also conducted on sea spray aerosols generated from Moreton Bay seawater samples in a laboratory-based bubble chamber. Accumulation mode sea spray particles (38-173 nm) were found to contain only a minor organic fraction (< 10%) that had little effect on particle hygroscopicity. These results are important because previous studies have observed that accumulation mode sea spray particles are predominantly organic (~80% organic mass fraction). The work presented here suggests that this is not always the case, and that there may be currently unknown factors that are controlling the transfer of organics to the aerosol phase during the bubble bursting process. Taken together, the results of this research program have significantly improved our understanding of organic-containing marine aerosols and the way they interact with water vapour in the atmosphere.

Keywords

Marine aerosols, water uptake, hygroscopic growth, VH-TDMA, atmospheric aerosols, organic aerosols, sea spray aerosols, sulphate aerosols, atmospheric new particle formation, nucleation events, nucleation mode, Aitken mode, accumulation mode, aerosol composition, volatility, HTDMA, deliquescence, water uptake suppression, organic films, bubble chamber.

List of publications

Modini, R. L., Ristovski, Z. D., Johnson, G. R., He, C., Surawski, N., Morawska, L., Suni, T., and Kulmala, M.: New particle formation and growth at a remote, sub-tropical coastal location. *Atmospheric Chemistry and Physics*, 9(19), 7607-7621, 2009.

Modini, R. L., Johnson, G. R., He, C., and Ristovski, Z. D.: Observation of the suppression of water uptake by marine particles. *Atmospheric Research*, In press, corrected proof online, 2010.

Ovadnevaite, J., Ceburnis, D., Plauskaite-Sukiene, K., **Modini, R.**, Dupuy, R., Rimselyte, I., Ramonet, M., Kvietkus, K., Ristovski, Z., Berresheim, H., and O'Dowd, C. D.: Volcanic sulphate and arctic dust plumes over the North Atlantic Ocean. *Atmospheric Environment*, 43(32), 4968-4974, 2009.

Modini, R. L., Harris, B., and Ristovski, Z. D.: The organic fraction of bubble generated, accumulation mode Sea Spray Aerosol (SSA). *Atmospheric Chemistry and Physics*, 10(6), 2867-2877, 2010.

Statement of original authorship

The work contained in this thesis has not been previously submitted for a degree or diploma at 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.

Signed:……………………………………

Date:………………………………...........

Acknowledgements

I would like to acknowledge and sincerely thank the following people who have helped make this research possible:

My soon-to-be wife, Marie Niccolini, who gave me love, support and understanding at every stage of this three-and-a-half year journey. It is no exaggeration to say that this thesis would not exist without Marie.

My principal supervisor, Associate Professor Zoran Ristovski, for being such a great mentor and friend. There simply isn’t enough room to list all the things Zoran has done to make this work possible. I have learnt many invaluable lessons under his guidance.

My associate supervisor, Dr Graham Johnson, who has also been a great mentor and friend.

My friends and colleagues in the International Laboratory for Air Quality and Health (ILAQH).

Contents

Chapter 1: Introduction

1.1 The Scientific Problem

Atmospheric aerosols have major environmental impacts related to global and regional climate and the hydrological cycle. Aerosols affect the Earth's climate both directly- through scattering and absorbing radiation- and indirectly by changing the properties of clouds. Overall it is predicted that aerosols cause negative radiative forcing of the Earth's energy budget (that is, they have a cooling effect on the Earth's surface). However, calculations of the magnitude of this forcing are much more uncertain than those for other important, comparable forcing agents (e.g. greenhouse gases) (Forster et al., 2007). As governments and policymakers stand poised to restructure entire economies in the name of global warming, it is imperative that scientific models provide accurate predictions of how warm the Earth will become. Part of this involves quantifying more precisely the effect aerosols have on the Earth's climate.

Water uptake refers to the ability of a particle to take up water vapour from the surrounding atmosphere. Under sub-saturated conditions (RH<100%) the resulting growth is termed hygroscopic growth. Water uptake is a property that affects particle size and phase and therefore influences many characteristics of an aerosol including its optical properties, atmospheric lifetime, ability to act as Cloud Condensation Nuclei (CCN) and chemical reactivity. This means water uptake is one of the key factors determining the direct and indirect effects of aerosols on climate. The hygroscopicity of a particle depends on its chemical composition. While the water uptake properties of atmospherically relevant inorganic salts as a function of relative humidity are generally well-known, the effects of organics on the water uptake of atmospheric aerosols are not yet fully understood. This is partly because atmospherically relevant data on the composition, relative concentrations and mixing states of organic and inorganic components are scarce for many important aerosol systems, and partly because organics can sometimes influence the hygroscopic growth of inorganic aerosols in complex and unexpected ways.

Organic compounds can comprise a significant and sometimes dominant fraction of all natural and anthropogenic aerosol types, including those produced over the ocean (e.g. O'Dowd et al., 2004). These are marine aerosols and they are the main focus of this research program. Marine organic aerosols have both primary and secondary production mechanisms. The primary mechanism occurs when organic material concentrated at the ocean surface is collected by rising bubbles which subsequently burst to generate sea salt aerosol enriched with organic matter. This is collectively known as sea spray aerosol. The secondary formation of marine organic aerosol results from the chemical processing of biogenic volatile organic compounds into condensable organic vapours that subsequently enter the aerosol phase.

Considering the global scale of marine aerosols- oceans cover ~70% of the Earth’s surface- observations of both primary and secondary marine organic aerosols are relatively scarce. Consequently their relative fractions and mixing states with the dominant inorganic marine particle types (sea salt, sulphates) are still not well known over a large range of oceanic and atmospheric conditions. This is especially true for the smallest but most numerous marine nanoparticles in nucleation ($3 \leq d_p \leq 25$ nm), Aitken ($20 \leq d_p \leq 80$ nm) or accumulation modes ($80 \leq d_p \leq 600$ nm). Accumulation mode particles are the main contributors to the direct (scattering) and indirect (cloud-related) effects of marine aerosols on climate, and the nucleation and Aitken modes are important starting points for this larger mode. Therefore, it is very important to accurately characterise the size distribution, composition, mixing state and resulting hygroscopic properties of the small but incredibly numerous marine aerosol particles covering a large portion of the Earth’s surface.

1.2 Overall aims of the study

The broad aim of this research program was to investigate how organics influence the hygroscopic growth of ultrafine marine aerosol particles ($d_p < \sim 200$ nm) using a Volatility-Hygroscopicity-Tandem Differential Mobility Analyser (VH-TDMA). Pursuit of this goal also involved investigation of the formation and composition of marine aerosols, and a number of other project aims were identified. Overall, these can be summarised as follows:

1) To examine the influence that organics have on the hygroscopic growth of marine aerosol particles sampled at remote, coastal sites

2) To investigate atmospheric new particle formation events in coastal environments, including examination of the conditions required for an event to occur, the frequency of event occurrence and the composition of freshly-formed nucleation mode particles ($d_p < 25$ nm)

3) To investigate the composition of aerosol particles in Aitken and lower-accumulation modes sampled at remote, coastal sites

4) To examine the size-resolved composition and hygroscopic properties of nascent sea spray aerosol particles generated from ocean water samples in a laboratory-based bubble chamber.

5) To further develop the VH-TDMA technique, particularly its ability to probe the chemical composition of ultrafine particles.

1.3 Specific objectives of the study

In order to achieve the aims of the study the following objectives were identified. This information is summarised graphically in Figure 1.1.

1) To conduct field measurements at a Pacific Ocean coastal site (Agnes Water, Australia). Specifically, to measure the physical characteristics (size distributions, concentrations) of ambient particles and ions arriving at the site to determine whether atmospheric new particle formation events occurred in the region, the frequency of such events and the conditions required for events to occur. In addition, we planned to measure the physicochemical characteristics of ultrafine particles arriving at the site with a VH-TDMA in order to:

a) Infer the composition of nucleation mode particles ($d_p < 25$ nm) during nucleation events to gain information on how they grow to climatically-relevant sizes ($d_p > \sim 40$ nm)

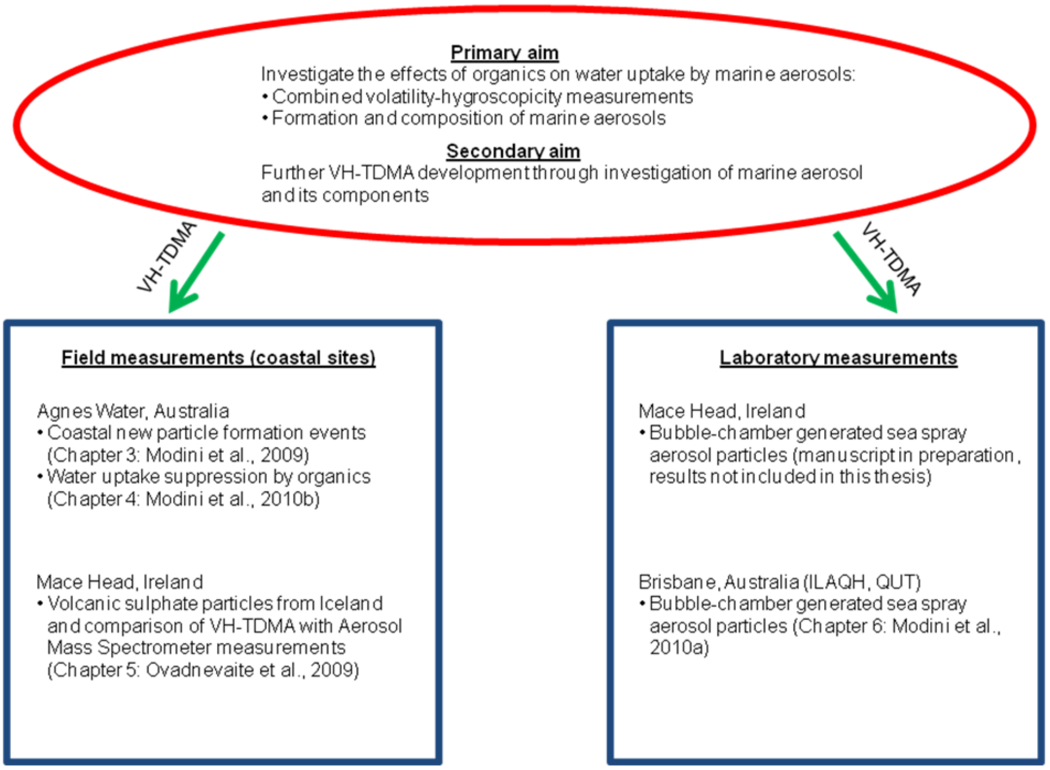
b) Investigate how organic aerosols affect the hygroscopic growth of particles arriving at the site in clean, marine air masses

This objective is addressed within two papers. The description and classification of nucleation events occurring at the Agnes Water site is described in Chapter 3. This section also describes the VH-TDMA characterisation of freshly-nucleated particles at Agnes Water and identifies particular chemical species that are responsible for particle growth. Chapter 4 characterises the hygroscopic properties of Aitken mode marine particles at Agnes Water, and analyses in detail the interesting way in which organic components can affect the hygroscopic growth of these aerosol particles.

2) To conduct measurements at an Atlantic Ocean coastal site (Mace Head, Ireland). In particular, to measure compositional properties of ultrafine aerosol particles with a VH-TDMA and compare the results with independent, real-time measurements of aerosol chemical composition obtained by an Aerosol Mass Spectrometer (AMS). This objective is addressed in Chapter 5. This section describes a unique day when volcanic sulphate emissions from Iceland were detected at Mace Head. The VH-TDMA was used to measure the degree to which the volcanic sulphate particles were neutralised by ammonia and the results were compared to AMS measurements.

3) To conduct measurements of sea spray aerosol particles generated from Moreton Bay seawater samples in a laboratory-based bubble chamber. Bubble chambers mimic the bubble bursting processes on ocean surfaces to generate nascent sea spray particles isolated from other aerosol types. The objective was to design and build a suitable bubble chamber, then characterise the size distribution, size-resolved organic fraction and

hygroscopic properties of particles generated from ocean water samples in the chamber. This objective is addressed in Chapter 6.



Primary aim

Investigate the effects of organics on water uptake by marine aerosols:
- Combined volatility-hygroscopicity measurements
- Formation and composition of marine aerosols

Secondary aim

Further VH-TDMA development through investigation of marine aerosol and its components

Field measurements (coastal sites)

Agnes Water, Australia
- Coastal new particle formation events (Chapter 3: Modini et al., 2009)
- Water uptake suppression by organics (Chapter 4: Modini et al., 2010b)

Mace Head, Ireland
- Volcanic sulphate particles from Iceland and comparison of VH-TDMA with Aerosol Mass Spectrometer measurements (Chapter 5: Ovadnevaite et al., 2009)

Laboratory measurements

Mace Head, Ireland
- Bubble-chamber generated sea spray aerosol particles (manuscript in preparation, results not included in this thesis)

Brisbane, Australia (ILAQH, QUT)
- Bubble-chamber generated sea spray aerosol particles (Chapter 6: Modini et al., 2010a)

Figure 1.1: Structure of the PhD research program

1.4 Account of the scientific continuity of the research papers

Through the intended investigation of the hygroscopic properties of mixed organic-inorganic marine particles, this research program has contributed substantially to the scientific knowledge of marine aerosols. It has provided valuable observations of relative fractions and mixing states of organic and inorganic components in primary (sea spray) and secondary ultrafine marine aerosols, and analysed the resulting hygroscopic properties of such aerosols.

A month-long field campaign was first conducted in March-April 2007 at Agnes Water, Australia. Frequent atmospheric new particle formation events were observed at the site. The events were described and classified in the first paper published as part of this research program (Modini et al., 2009). It was concluded that the precursor vapours responsible for particle formation were most likely of marine/coastal origin. A unique feature of the study was the investigation of the chemical composition of freshly-nucleated particles (17–22.5 nm) with a VH-TDMA. This is a significant achievement because only a few state-of-the-art measurement approaches are able to probe the composition of aerosol particles with such small diameters. The majority of the volume of the nucleation mode particles was confidently attributed to sulphate and organic components. Therefore, it was concluded that the condensation of sulphate and/or organic vapours was most likely responsible for growth of freshly nucleated particles to climatically relevant sizes in the coastal region surrounding Agnes Water.

A second paper that came out of the Agnes Water campaign focussed on the hygroscopic properties of slightly larger, Aitken mode particles that were observed in clean, marine air masses (Modini et al., 2010b). Specifically, the paper reported the observation of volatile organic components that caused suppression of hygroscopic growth (not merely a decrease in hygroscopic growth). Similar effects have only been observed rarely in both natural and polluted environments (Chuang, 2003; Johnson et al., 2005; Roberts et al., 2010; Villani et al., 2009) so this was an important result. It was suggested that water uptake suppression was the result of either organic films that slowed the rate of hygroscopic growth or organic-inorganic interactions in solution that had a negative effect on hygroscopicity.

A second month-long measurement campaign was conducted in June 2007 at Mace Head Atmospheric Research Station on the west coast of Ireland. High concentrations of sub-micrometer marine organic aerosols are typically observed at this site in summer (O'Dowd et al., 2004). We planned to investigate the physicochemical properties of these ocean-derived organics with a VH-TDMA to determine how they influence particle hygroscopicity. Unfortunately, very little organic material was detected by the VH-TDMA during the campaign. However, another interesting result came out of the measurements. On one unique day large sulphate loadings were observed by an Aerosol Mass Spectrometer (AMS). These were identified as volcanic emissions from Iceland that had travelled for at least 3 days over the North Atlantic Ocean to Mace Head. The AMS and VH-

TDMA were operating in parallel during the event so it provided an excellent opportunity to test the ability of the VH-TDMA to infer particle composition. This was achieved by comparing its measure of the degree to which the volcanic sulphate particles were neutralised by ammonia with the corresponding AMS measurements. Both instruments observed that the sulphate particles were only partially neutralised and differences in the calculations could be explained by particle size (Ovadnevaite et al., 2009). This was an important verification of the VH-TMDA's ability to infer particle composition based on the simultaneous measurement of aerosol volatility and hygroscopicity.

A series of laboratory-based bubble chamber experiments were also conducted during the Mace Head campaign to investigate the size-resolved composition of sea spray particles produced from North Atlantic Ocean water. A manuscript containing the results of these experiments is currently in preparation with researchers from the National University of Ireland, the Institute of Atmospheric Sciences and Climate- Italian National Research Council and the Institute of Physics Lithuania. Due to delays in the joint preparation of this manuscript the results could not be included as part of this thesis. However, following the Mace Head campaign further bubble chamber experiments were conducted at QUT with water samples from Moreton Bay. A bubble chamber was first designed and constructed then shown to produce sea spray particles broadly consistent with previous studies. The volatile and hygroscopic properties of the particles were then investigated with a VH-TDMA. The results suggested that the accumulation mode sea spray particles (38–173 nm) produced in the bubble chamber contained only a minor organic fraction that had little effect on hygroscopic growth (Modini et al., 2010a). This result was surprising because previous studies had found accumulation mode sea spray particles were dominated by organics (Facchini et al., 2008b; Keene et al., 2007a). Our measurements suggest that this is not always the case.

Chapter 2: Literature review

2.1 Introduction

Atmospheric aerosols affect the Earth's climate both directly, through scattering and absorbing radiation, and indirectly by changing cloud properties such as cloud cover, vertical extant, reflectance, ability to precipitate and lifetime (Forster et al., 2007). Overall it is predicted that aerosols cause negative radiative forcing of the Earth's energy budget, although there is significant uncertainty in the estimates of the magnitude of this forcing especially in regards to the aerosol indirect (cloud) effect. Related to their climatic impacts, aerosols also affect the hydrological cycle, which in turn affects the world's fresh water supply (Ramanathan et al., 2001). Atmospheric aerosols also impact human health via the inhalation of particles (Pope and Dockery, 2006).

To predict the abundance of aerosol particles it is necessary to characterise their emission sources, transformations in the atmosphere and removal rates. Additionally, in order to comprehend the direct and indirect climatic effects of atmospheric aerosols and their impact on human health it is necessary to understand their size-dependent composition, mixing states, optical properties, hygroscopic properties and ability to act as cloud condensation nuclei (CCN). Currently, this knowledge is not complete for many important aerosol systems, including marine aerosols. Therefore, this research program was directed towards marine aerosols, with a particular emphasis placed on their water uptake properties. This chapter critically reviews the literature concerning these two themes, links them together, identifies gaps in knowledge and explains how these relate to the research program.

2.2 Marine aerosols

2.2.1 Introduction

Boundary layer air masses that have spent at least 4–5 days over oceanic regions support aerosol populations whose physical and chemical characteristics are distinct from those of aerosols observed in continentally affected air masses. Marine aerosol particles have relatively low and stable number concentrations, generally in the range 200–800 cm^{-3} (Fitzgerald, 1991; Heintzenberg et al., 2000; O'Dowd and De Leeuw, 2007). This stability implies that there are natural sources of marine aerosols constantly replenishing the particles lost due to wet and dry deposition. These include the primary production of sea spray particles, the entrainment of particle rich air from the free troposphere (FT) and the secondary production of non sea salt (nss)-sulphate and secondary organic aerosol (SOA). In addition, emissions from marine anthropogenic activities such as shipping can add significantly to the background marine aerosol (Capaldo et al., 1999). Persistent continental particles such as mineral dust also contribute.

Marine aerosols are one of the most globally important aerosol systems because oceans cover over two-thirds of the Earth’s surface. In the vast volume of marine boundary layer (MBL) air, marine particles affect radiative transfer by scattering and absorbing radiation (Hoppel et al., 1990; Murphy et al., 1998; Quinn and Bates, 2005; Quinn and Coffman, 1999) and acting as the seeds (CCN) upon which cloud droplets form (Charlson et al., 1987; O'Dowd and Smith, 1993; Pierce and Adams, 2006; Woodcock, 1952). In addition, marine aerosols participate in a large range of chemical reactions that affect important biogeochemical cycles and influence the air quality in populous coastal areas (Finlayson-Pitts and Hemminger, 2000; Keene et al., 2007b; McFiggans et al., 2000; O'Dowd et al., 1997; Osthoff et al., 2008) and even inland locations (Thornton et al., 2010).

2.2.2 Marine aerosol size distribution

Thousands of marine aerosol number size distributions have been measured over the last few decades and a consistent, bi-modal picture has emerged. Marine particles vary in size over 6 decades from a few nanometres to hundreds of micrometres. However, most marine particles are concentrated in 2 dominant modes (e.g. Fitzgerald, 1991; Heintzenberg et al., 2004; Heintzenberg et al., 2000; Hoppel et al., 1990; O'Dowd et al., 1997; Quinn et al., 1996 and references therein). One peak is commonly centred around 30–50 nm and covers the size range from 20 to 80 nm. This is known as the Aitken mode. A second peak known as the accumulation mode is typically centred around 150–200 nm and covers the size range 80–600 nm. These modal definitions vary from study to study. This is partly because the exact positions and widths of the modes vary geographically and even seasonally. For example, the average size distribution of particles sampled in North Atlantic Ocean air masses at Mace Head, Ireland during winter consists of an Aitken mode centred at 31 nm and an accumulation mode centred at 103 nm. During summer these average geometric mean diameters (GMDs) increase to 49 nm and 177 nm for the Aitken and accumulation modes, respectively (Yoon et al., 2007).

The shape of the marine aerosol number size distribution is relatively stable because Aitken and accumulation mode particles have relatively long atmospheric lifetimes. Smaller particles diffuse quickly and grow rapidly into an Aitken mode due to coagulation and condensation while larger particles are subject to significant sedimentation losses. It is generally accepted that the split between the Aitken and accumulation modes and the resulting minimum in marine particle size distributions around 80 nm is due to repeated in-cloud processing cycles (Hoppel et al., 1990; Hoppel et al., 1986). This process works as follows. At typical supersaturation values that occur in the MBL (0.1–0.3%) (Hegg et al., 2009; Hudson and Li, 1995) soluble particles larger than about 80 nm will activate into cloud droplets. Aqueous phase reactions within cloud droplets can convert trace gases into non-volatile material that remains in the particle phase when the cloud evaporates (as ~90% of clouds do). For example SO_2 can be oxidised and converted into sulphate aerosol via such a mechanism. In addition, smaller interstitial particles that didn’t activate can diffuse and collide with larger cloud droplets. Following cloud evaporation, both of these mechanisms serve to increase the size of activated particles and a minimum forms in the marine aerosol size distribution around 80nm. This minimum is deepened by repeated cloud formation and evaporation cycles; it is thought 10–20 of these cycles could occur in the ~week-long lifetime of a marine aerosol particle (Hoppel et al., 1990). The minimum is sometimes referred to as the Hoppel minimum after the primary author who first identified and explained it.

A third mode is sometimes observed in marine aerosol number size distributions. This mode contains particles that have just formed or nucleated in the atmosphere and is therefore referred to as a nucleation mode. It can extend from sizes where particle formation occurs, 1–3 nm, right up until 20–25 nm where nucleation mode particles then merge into an Aitken mode. Nucleation modes have been observed rarely in the remote MBL but frequently in coastal environments. This topic is discussed in more detail in section 2.2.7.

The volume or mass size distribution of marine particles looks very different to their number size distribution. This is because about 95% of marine aerosol mass is contributed by large, super-micrometre particles that make up only ~5% of total particle numbers (Fitzgerald, 1991). These particles form a coarse mode (GMD > 1 μm) which is barely visible in number size distributions but dominant in mass or volume size distributions. In regions free from continental influence and mineral dust the marine aerosol coarse mode is dominated by sea salt particles and is therefore very sensitive to wind speed (see section 2.2.3 below). Coarse mode particles can contribute significantly to the direct effect of marine aerosols on climate (Quinn and Coffman, 1999). However, their contribution to the indirect (cloud) climate effects is limited by their small number concentrations and therefore small contributions to CCN numbers. Having said that, coarse mode particles activate very readily and this means they may have disproportionately large effects on cloud microphysics and precipitation formation. These are so-called ‘Giant CCN’ effects (Andreae and Rosenfeld, 2008 and references therein).

2.2.3 Primary marine aerosol: formation and physical properties

The primary production of marine aerosol occurs due to wind stress on the ocean surface. Sea spray droplets are emitted when air bubbles rise to the surface behind breaking waves and burst or they are simply torn from the crests of waves. Sea spray aerosol (SSA) particles are formed when these droplets evaporate. Boyce first explicitly suggested that the majority of sea salt particles were emitted to the atmosphere by small bubbles bursting on seawater surfaces and not by mechanical dispersion from breaking waves (Boyce, 1951), although

Woodcock hinted at this idea a few years earlier (Woodcock, 1948). Both authors drew inspiration from Stuhlman who demonstrated the production of droplets from bursting bubbles in an early laboratory study (Stuhlman, 1932). Woodcock further supported the hypothesis with the publication of comprehensive sea salt size distribution data showing a clear trend of increasing salt concentration with increasing wind speed, which he suggested was a result of increased bubble production as wind speed increased (Woodcock, 1953). It is now estimated that bubble bursting processes on ocean surfaces generates a flux of roughly 10 Pg or 1.2×10^{27} particles of SSA to the atmosphere every year (Andreae and Rosenfeld, 2008). This is the largest mass emission flux to the atmosphere of all aerosol types, natural or anthropogenic.

Droplets produced from bursting bubbles are usually classified as film drops or jet drops (Blanchard, 1989). Film drops are generated when fragments of bubble film (cap) are ejected into the air as a bubble bursts. Secondary droplets may also be created when some of these fragments collide with the air-water surface (Spiel, 1998). Milliseconds after a bubble burst (Spiel, 1995) jet drops are generated from the break-up of the upward moving jet column caused by the collapse of the bubble cavity. Jet drops are in the super-micrometre size range: they are roughly one tenth the size of their parent bubbles (Blanchard, 1989). A single bursting bubble can produce a few jet drops and hundreds of film drops. Aside from bubble bursting, the other mechanism of sea spray droplet production is the tearing of very large droplets (> 20 μm) from wave crests at high wind speeds. These are known as spume droplets (e.g. Kudryavtsev and Makin, 2009). It appears that following evaporation, film drops produce accumulation and coarse mode SSA particles, jet drops produce even larger coarse mode particles and spume drops produce even larger particles that can reach sizes greater than 100 μm (O'Dowd et al., 1997).

Bubble formation in the ocean mainly occurs due to breaking waves, although other production pathways exist such as falling rain and snow or sudden increases in gas supersaturation due to photosynthesis or temperature changes (Blanchard, 1989). The properties (e.g. size distributions) of bubbles formed due to the dominant breaking wave mechanism have been studied fairly extensively (e.g. Deane and Stokes, 2002; Leifer et al., 2006; Leifer and de Leeuw, 2006). If waves are steep enough they will produce dense bubble plumes that form foams on the ocean surface. These are known as whitecaps. Whitecap formation, and therefore significant SSA production, doesn't occur for wind speeds less than about 3 or 4 m s^{-1}. A number of parameterisations of size-resolved SSA production (flux) as a function of whitecap coverage and/or wind speed have been developed using a variety of independent measurement and modelling techniques. These are known as sea spray source functions and they commonly have a power-law dependence on wind speed, meaning sea spray production increases in greater proportion to increases in wind speed as it gets stronger (Monahan and Muircheartaigh, 1980; O'Dowd and De Leeuw, 2007). At wind speeds greater than about 7–11 m s^{-1} spume droplet generation also occurs (e.g. Andreas, 1998) and the mass emission of sea spray aerosol increases dramatically. Sea salt mass concentrations up to 1000 μg m^{-3} have been measured at wind speeds greater than 20 m s^{-1} (Lewis and Schwartz, 2004).

Size-resolved SSA source functions have been reviewed considerably in recent years (e.g. Andreas, 1998; Clarke et al., 2006; Lewis and Schwartz, 2004; O'Dowd and De Leeuw, 2007) and their comparisons and areas of divergence will not be discussed in further detail here. Of interest however are the recent discoveries of sea spray aerosol production down to very small diameters. Traditional source functions focused on large accumulation mode (d_p > 500 nm) or super-micrometre sea spray particles partly because these were of interest in studies of the sea-air transfer of heat and moisture (e.g. Andreas, 1998) and partly because this was all that the technology allowed. However, field observations of sub-micrometre sea salt particles with diameters down to 35 nm (Murphy et al., 1998; O'Dowd and Smith, 1993; Zhou et al., 2001) motivated the extension or extrapolation of source functions to smaller particle diameters (Gong, 2003; Vignati et al., 2001). A number of laboratory bubble chamber studies then confirmed the existence of ultrafine sea spray particles through the detection of dominant accumulation modes (GMD ~ 100 nm) in nascent SSA number size distributions (Fuentes et al., 2010; Hultin et al., 2010; Keene et al., 2007a; Martensson et al., 2003; Modini et al., 2010a; Sellegri et al., 2006; Tyree et al., 2007). Size-resolved source functions that cover sea spray particles as small as 10 nm have now been derived from state-of-art laboratory (Martensson et al., 2003) and field measurements (Clarke et al., 2006; Nilsson et al., 2007).

The discovery that ocean bubble bursting processes result in the formation of large numbers of accumulation mode sea spray particles is critically important for efforts to model the climatic effects of marine aerosols. Accumulation mode particles (0.1–1 μm) are the most efficient at scattering light per unit aerosol mass (Quinn et al., 1996; Schwartz, 1996) and it has been shown that sub-micrometre sea salt particles contribute significantly to the direct effect of marine aerosols on climate (Murphy et al., 1998; Quinn and Coffman, 1999). In addition, sea spray particles are efficient cloud condensation nuclei (Fuentes et al., 2010). Therefore, at high wind speeds the SSA accumulation mode contributes significantly to marine CCN numbers and the indirect effects of marine aerosols on climate (Clarke et al., 2006; O'Dowd et al., 1997; Pierce and Adams, 2006), in contradistinction to what was believed 20 years ago when nss-sulphates were thought to control these effects (Charlson et al., 1987)[1]. For example, it has been estimated that sea spray particles represent 52–91% of the remote marine CCN population at a wind speed of 15 m s^{-1} (Clarke et al., 2006). It has also been shown that excluding the very small ultrafine sea spray particles (d_p < 100 nm) from a detailed marine aerosol model can cut its predicted CCN (at 0.2% supersaturation) concentrations over the Southern Ocean by almost half (Pierce and Adams, 2006). Therefore, it is very important to consider the large numbers of accumulation mode SSA particles, including those in the ultrafine particle size range, when investigating the climatic impacts of marine aerosol.

---

[1] However even earlier than this, for most of the 20th century, sea salt was assumed to be the dominant natural source of marine CCN, although this was questioned and disputed by a number of studies (see Hobbs, P. V.: Q. J. Roy. Meteor. Soc., 97(413), 263-271, 1971, and references therein).

2.2.4 Primary marine aerosol: composition

As well as size, the composition of sea spray aerosol is also climatically important. The composition determines the size of SSA particles as a function of RH (Ming and Russell, 2001) and therefore their scattering potential (Randles et al., 2004), their CCN efficiency (Fuentes et al., 2010; Moore et al., 2008) and also their role in atmospheric chemistry (Finlayson-Pitts and Hemminger, 2000; Smoydzin and von Glasow, 2007; Zhou et al., 2008). SSA consists of both an inorganic (sea salt: Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, Br^-, plus other trace ions) and organic fraction, which is why it should be referred to as sea spray aerosol and not simply sea salt aerosol. The relative fractions of the inorganic ions in nascent sea salt aerosol (i.e. with no atmospheric processing) are the same as the corresponding fractions for sea salt in ocean water, except for Ca^{2+}, which appears to be enriched in the aerosol phase (Keene et al., 2007a; Sievering et al., 2004).

The SSA organic fraction was detected decades ago in novel experiments conducted on the coast of Hawaii (Blanchard, 1964). More quantitative field measurements of marine organic aerosols (Cavalli et al., 2004; Matsumoto et al., 1997; Middlebrook et al., 1998; Novakov et al., 1997; O'Dowd et al., 2004; Putaud et al., 2000) have reignited interest in sea spray organics in recent years. Observations indicate that organic fraction of aggregate or sub-micrometre SSA is tens to thousands of times greater than the organic fraction of its seawater source (Gershey, 1983; Hoffman and Duce, 1976; Russell et al., 2010). This is because rising air bubbles in the ocean collect organic matter and transport it to an enriched layer of chemical and biological material at the ocean surface known as the sea-surface micro-layer (Liss and Duce, 1997). Organic material, and in particular surface-active organic material, becomes concentrated at the sea-surface micro-layer by factors of up to 10 compared to sub-surface waters (Hunter, 1997). When bubbles reach this layer and subsequently burst the emitted spray droplets are even further enriched with organics.

The precise composition of the SSA organic fraction is still not completely defined. Classes of organic compounds such as saccharides, lipids, alcohols, esters, amino acids and amines have all been directly observed in artificially-generated SSA (Facchini et al., 2008b; Gershey, 1983; Kuznetsova et al., 2005) or observed in correlation to sea salt tracers (e.g. Na) in ambient marine aerosol (Mochida et al., 2002; Russell et al., 2010). Organics may be internally mixed with sea salt particles (Modini et al., 2010a; Russell et al., 2010) or be part of bacteria, viruses and transparent-exopolymer-gels, all of which are enriched in aggregate sea spray (Aller et al., 2005; Bigg and Leck, 2008; Blanchard, 1989). The SSA organic fraction appears to be mainly insoluble during phytoplankton bloom conditions (Facchini et al., 2008b) but soluble at other times (Russell et al., 2010). Depending on concentration (determined in the atmosphere by the amount of condensed water) marine organics can decrease the surface tension of SSA droplets by up to 25 mN m^{-1} (Cavalli et al., 2004; Facchini et al., 2008b; Moore et al., 2008).

Decades ago it was hypothesised that the organic fraction of SSA may increase with decreasing particle size (Barker and Zeitlin, 1972; Hoffman and Duce, 1974). Recent modelling (Oppo et al., 1999) and bubble-chamber studies including off-line chemical analyses of size-resolved impactor samples (Facchini et al., 2008b; Keene et al., 2007a) suggest that this is indeed the case. The Keene and Facchini studies both found that organics formed only a minor fraction (< ~10%) of super-micrometre particles but dominated the mass (up to 80%) of accumulation mode SSA particles generated in bubble chambers filled with oligotrophic (Keene) and productive (Facchini) ocean water samples (note that this means organics in super-micrometre particles were still enriched hundreds of times relative to seawater organics because seawater organic concentrations are low compared to sea salt concentration, typically 1–10 mg L^{-1}). Based on these studies and similar results from impactor measurements conducted at Mace Head, Ireland (Cavalli et al., 2004; Facchini et al., 2008b; O'Dowd et al., 2004), an expectation has arisen that accumulation mode SSA particles are predominantly organic with only a minor saline contribution (e.g. Andreae and Rosenfeld, 2008).

Bigg and Leck go even further to suggest that the particles comprising the SSA accumulation mode (< 200 nm) are actually organic fragments with no inorganic component at all (Bigg and Leck, 2008). This suggestion is based on: 1) speculative questioning of the independent lines of evidence[2] supporting the existence of sea salt in accumulation mode marine aerosol, and 2) transmission electron microscopy investigations of marine biogenic organic aerosol particles (e.g. exopolymer gels, microcolloid aggregates, microorganisms and their fragments) in accumulation mode aerosols sampled in the Arctic (Bigg and Leck, 2001; Leck and Bigg, 2005b,a; Leck et al., 2002), over the Great Barrier Reef (Leck and Bigg, 2008), at Cape Grim, Tasmania (Bigg, 2007) and Mace Head, Ireland (Bigg and Leck, 2008). Similar particles have been observed in the sea surface microlayer (Aller et al., 2005; Bigg et al., 2004) and Bigg and Leck suggest they are aerosolised by bursting bubbles in the same manner as described for SSA above. While electron microscopy provides strong evidence for the existence of purely organic, biogenic aerosol particles it isn’t a suitable method for determining the relative abundance of such particles. Considering all the evidence to the contrary, it is therefore very doubtful that sea salt is excluded during the bubble bursting process and only biogenic organic particles are emitted in sea spray droplets, as suggested by Bigg and Leck (2008).

Considering the complexity and possible diversity of the chemical composition of sea spray aerosol, it is necessary to include compositional information in a size-resolved SSA source function in order to correctly model its climatic influence. O’Dowd and colleagues have taken the first step in this direction with the development of a combined organic-inorganic sub-micrometre SSA source function (O'Dowd et al., 2008) that has already been applied in models (Gantt et al., 2010; Vignati et al., 2010). One input into this source function is the organic mass fraction of sub-micrometre SSA as a function of oceanic chlorophyll *a* (chl *a*) concentration. This was derived from ambient measurements conducted at Mace Head, Ireland, where a correlation between marine (water insoluble)

---

[2] E.g. thermal stability, chemical analysis of impactor samples, scanning electron microscopy with x-ray analysis, aerosol mass spectroscopy, hygroscopicity and bubble chamber studies

organic aerosol concentration and satellite-derived surface chl *a* has been observed (Yoon et al., 2007). Future studies need to derive similar combined organic-inorganic SSA source functions for other oceanic regions, and determine whether oceanic chl *a* is the best predictor of SSA organic fraction, or whether another variable such as oceanic dissolved organic carbon concentration (DOC) is more suitable.

2.2.5 Secondary marine aerosol: non sea salt (nss)-sulphate

As well as the primary sea spray source, marine aerosols can also form in the atmosphere from gas-to-particle conversion processes, namely condensation and nucleation. These particles are collectively known as secondary marine aerosols. The most abundant of these are non sea salt (nss)-sulphates, which are neutralised to varying degrees by ammonia (i.e. they exist in forms ranging from sulphuric acid, H_2SO_4, to ammonium sulphate, $(NH_4)_2SO_4$). Nss-sulphate is a major and often dominant component of sub-micrometre marine aerosol (e.g. Fitzgerald, 1991; O'Dowd et al., 1999; Quinn et al., 2000). It is derived from the photo-oxidation products of sulphur-containing gases emitted from both anthropogenic and natural activities. The main anthropogenic precursor in the marine environment is sulphur dioxide (SO_2) carried in continental outflow and emitted along major shipping routes (Capaldo et al., 1999). The natural sources include sulphurous volcanic emissions (von Glasow et al., 2009), which are a potentially large but intermittent source, and oceanic sources of biogenic sulphur vapours. The dominant biogenic marine source is dimethylsulphide (DMS) (Charlson et al., 1987) which is produced from dimethylsulphoniopropionate (DMSP) synthesised by phytoplankton. Anthropogenic emissions can contribute significantly to marine nss-sulphate concentrations in the more populated and polluted northern hemisphere, while biogenic sources are the dominant contributors in the sparsely filled southern hemisphere, particularly over the pristine Southern Ocean (Bates et al., 1992; Capaldo et al., 1999; Chin and Jacob, 1996).

In the atmosphere DMS is oxidised by the OH radical, the NO_3 radical or halogens to produce a complex range of species including dimethyl sulphoxide

(DMSO), dimethyl sulphone ($DMSO_2$), methane sulphonic acid (MSA) and SO_2 (Barnes et al., 2006; von Glasow and Crutzen, 2004). All of these products can condense on existing aerosols and thereby increase their mass. However, only SO_2 can be further oxidised to form gaseous H_2SO_4, which can potentially form new atmospheric particles via binary H_2SO_4-H_2O nucleation (Kulmala et al., 1998) or ternary H_2SO_4-NH_4-H_2O nucleation (Kulmala et al., 2002). This is an important distinction because it means an increase in DMS emissions can potentially lead to an increase in the number of marine CCN, which could potentially increase the reflectivity of marine clouds.

This process was highlighted by Charlson, Lovelock, Andreae and Warren in 1987 when they famously postulated that it could form a climate-stabilising negative feedback loop, whereby any temperature induced changes in phytoplankton (and DMS) levels would be self-regulated by counteracting changes modulated by cloud reflectivity (Charlson et al., 1987). This is known as the CLAW hypothesis after its author's names. While today this still unproven hypothesis is considered qualitatively possible but generally far too simplistic, the original CLAW paper is lauded as the beginning of the multi-disciplinary field of Earth Systems Science and it has been cited in nearly 1800 publications. A detailed overview of the current thinking on CLAW can be found in a special issue of the journal *Environmental Chemistry* (Volume 4 number 6 2007).

One of the issues with the CLAW hypothesis is that observations of new particle formation in the remote MBL (i.e. non-coastal) have been rare (Heintzenberg et al., 2004), and only one example has been adequately linked to local DMS emissions (Clarke et al., 1998a). In addition, modelling studies have shown that under typical conditions in the MBL, DMS-related nucleation events should only occur rarely (Katoshevski et al., 1999; Pirjola et al., 2000; Yoon and Brimblecombe, 2002). This is because gaseous SO_2 and H_2SO_4 are readily scavenged by pre-existing aerosol before new particle formation can occur; scavenging mechanisms include condensation and aqueous phase oxidation in sea spray or cloud droplets (Cainey and Harvey, 2002; Hoppel et al., 1990; Sievering et al., 1992; Sievering et al., 2004). Therefore, nucleation can only occur when the condensational sink is low relative to the precursor source strength, for example in pristine arctic air or immediately following a precipitation event. A consequence of this consideration is that a large proportion of nss-sulphates in the MBL are likely to be internally mixed with existing marine aerosol, such as sea spray particles (Murphy et al., 1998). It also implies that the effect of DMS emissions on MBL CCN is limited to an increase in their size and activation efficiency, not an increase in their number as originally proposed in CLAW.

However, above the MBL, in the free troposphere (FT), the cooler and potentially cleaner conditions are much more conducive to DMS-related nucleation. Nucleation events have been observed in the clean outflow of clouds during aircraft flights (Clarke and Kapustin, 2002; de Reus et al., 2001; Perry and Hobbs, 1994; Zaizen et al., 1996) as well at surface-level following the entrainment of freshly nucleated particles from the free troposphere due to deepening of the well-mixed MBL or dynamic weather events such as the passage of cold fronts (Bates et al., 1998; Clarke et al., 2006; Covert et al., 1996; Jimi et al., 2008). It appears that freshly formed FT aerosol is primarily sulphate (Clarke and Kapustin, 2002; Clarke et al., 1999; Clarke et al., 1998b), which is potentially derived from the photo-oxidation of oceanic DMS carried aloft, although other species such as organics may also contribute (Swietlicki et al., 2000; Van Dingenen et al., 1999). FT entrainment is now recognised as one of the main sources of MBL particles (Clarke et al., 2006; Katoshevski et al., 1999; Raes, 1995; Van Dingenen et al., 1999). Indeed it is most likely responsible, along with primary SSA emissions, for the remarkable stability of marine aerosol number concentrations. Therefore DMS emissions may still have a large influence on marine CCN, although in a more complex way than first envisioned in CLAW.

2.2.6 Secondary marine aerosol: secondary organic aerosol (SOA)

Natural organic aerosols can also be formed by secondary processes in the marine atmosphere. Marine secondary organic aerosol (SOA) results from the chemical processing of biogenic volatile organic compounds (BVOCs) into condensable organic vapours that subsequently enter the aerosol phase, probably through condensation rather than nucleation. The most dominant form of marine SOA is methane sulphonic acid (MSA), formed from the oxidation of DMS (see section 2.2.6). Other species include alkylammonium salts such as dimethylammonium (DMA^+) and diethylammonium, (DEA^+) (Facchini et al., 2008a; Gibb et al., 1999; Muller et al., 2009; Rinaldi et al., 2010; Sorooshian et al., 2009) and dicarboxylic acids such as oxalic, malonic and succinic acid (Claeys et al., 2010; Muller et al., 2010; Rinaldi et al., 2010; Wang et al., 2006). In addition, isoprene and monoterpenes are known to be emitted by various plankton species and these have the potential to form SOA (Bonsang et al., 1992; Meskhidze and Nenes, 2006; Yassaa et al., 2008).

Models and observations indicate that biogenic SOA generally only makes up a very minor fraction of the total marine aerosol mass (Arnold et al., 2009; Claeys et al., 2010; Gantt et al., 2009). Although, large proportions (~10–30%) of water soluble organic matter (WSOM) have been observed in marine aerosols detected at Mace Head during summer (O'Dowd et al., 2004; Rinaldi et al., 2010; Yoon et al., 2007) and two independent studies suggest that WSOM at this site is predominantly formed in the atmosphere (i.e. it is SOA) (Ceburnis et al., 2008; Facchini et al., 2008b). Marine SOA (including MSA) generally exhibits a clear seasonality (Arnold et al., 2009; Facchini et al., 2008a; Mukai et al., 1995; Rinaldi et al., 2010; Sciare et al., 2009; Yoon et al., 2007), similar to biogenic nss-sulphate (Ayers et al., 1991; Savoie et al., 2002; Yoon et al., 2007), with high concentrations observed in spring-summer and low concentrations observed in winter. This is because marine biogenic vapours are produced and photo-oxidised more readily in the warmer, brighter and more biologically active spring and summer months (e.g. Sciare et al., 2000a; Sciare et al., 2000b).

2.2.7 Secondary marine aerosol: coastal nucleation events

In contrast to the remote MBL, new particle formation events are frequently observed in coastal areas where clean marine air meets high levels of anthropogenic oxidants. For example, nucleation events have been observed at coastal or near-coastal sites on the West coast of Ireland (O'Dowd et al., 2002b) and Scotland (Aitken, 1897), East coast of the UK (Coe et al., 2000), North West coast of France (McFiggans et al., 2010), Baltic Sea (Hyvarinen et al., 2008; Plauskaite et al., 2010; Ulevicius et al., 2002), Canary Islands (Rodriguez et al., 2008), East (e.g. Russell et al., 2007) and West coast (e.g. Wen et al., 2006) of the USA, West coast of Korea (Lee et al., 2008), East coast of China (Gao et al., 2009), East coast of Australia (Johnson et al., 2005; Mejia and Morawska, 2009; Modini et al., 2009), North West coast of Tasmania (Gras et al., 2009) and in the Arctic (Svalbard) (Strom et al., 2009) and Antarctic (Asmi et al., 2010). Many of the above studies did not identify a source of particle precursors or they concluded that the particle precursors had continental (e.g. forest), anthropogenic (including shipping) or remote marine (with particle formation aloft in the FT) origin. Only a small number of the observed coastal events have been directly and comprehensively linked to local coastal biogenic emissions, most notably those occurring at Mace Head, Ireland (O'Dowd et al., 2002b) and Roscoff, France (McFiggans et al., 2010).

Very strong new particle formation events have been observed on almost a daily basis for nearly 20 years at Mace Head (McGovern et al., 1996). The events are characterised by the appearance of a nucleation mode peaking between 3–10 nm and they correlate with low tide and high solar irradiance (O'Dowd et al., 2002a). Dynamic modelling combined with precursor gas concentration measurements (O'Dowd and Hoffmann, 2005 and reference therein), TEM analysis (Mäkelä et al., 2002) and hygroscopic growth factor measurements (Väkevä et al., 2002) indicate that sulphuric acid does not drive the particle production seen at this site, although it probably participates to some degree in the initial formation of stable atmospheric clusters (Kulmala et al., 2002) and the condensational growth of nucleation mode particles (O'Dowd and Hoffmann, 2005).

Rather, a series of chamber and modelling studies have identified iodine-containing compounds emitted by exposed macroalgae- firstly an organoiodine compound, diiodomethane (CH_2I_2) (Hoffmann et al., 2001; Jimenez et al., 2003), and later molecular iodine (I_2) (McFiggans et al., 2004; Saiz-Lopez et al., 2004)- as possible particle precursor vapours. These compounds can be photolysed in the presence of ozone (O_3) to form condensable iodine oxides (HOI, OIO, I_2O_2) that can drive particle formation. After some debate regarding the relative importance of CH_2I_2 and I_2 to the nucleation events observed at Mace Head (McFiggans, 2005; O'Dowd et al., 2005) it has been confirmed that I_2 is the dominant driver (Pirjola et al., 2005; Saiz-Lopez et al., 2006). Thus, the chain of events leading to observable particle formation at Mace Head can be summarised as follows: iodine-containing compounds (primarily I_2) are emitted by exposed macroalgae at low tide; in the presence of solar radiation and ozone these compounds are rapidly photolysed to condensable iodine oxides, which then drive the particle formation and growth processes, probably with help from sulphuric acid. Secondary organic aerosols may also contribute to particle growth (Vaattovaara et al., 2006).

A very recent and comprehensive field study has shown that this mechanism of particle formation also occurs on a regular basis at Roscoff on the North West coast of France (McFiggans et al., 2010). Further field studies are required to determine whether iodine-mediated particle formation also occurs at other coastal locations, particularly those in tropical or polar climate zones with oceanic and atmospheric conditions that differ substantially from those found at the temperate mid-latitude sites of Mace Head and Roscoff. In addition, future studies need to investigate whether molecular iodine and iodocarbons are emitted to the atmosphere in significant quantities on an ocean-wide scale by, for example, microscopic phytoplankton. This will determine if iodine-related particle production occurs in open ocean as well as coastal environments. An initial modelling exercise suggests that condensable iodine oxides are present in high enough quantities over the remote ocean to enhance particle production (O'Dowd et al., 2002c). However, the rarity of observed MBL nucleation events (Heintzenberg et al., 2004) suggests otherwise.

Another interesting region where coastal nucleation events might occur is coral reefs. A series of measurements in the 1970s suggested that the 2600 km long Great Barrier Reef (GBR) in Australia might be a significant source of new particles and/or their precursors (Bigg and Turvey, 1978). Variably high particle number concentrations (median = 1590 cm^{-3}) were observed on flights over the GBR, while significantly lower concentrations (median = 640 cm^{-3}) were observed over the seaward side of the reef. As a result, the authors estimated a reef-related particle emission/formation rate of 10^{19} s^{-1} along the 1000 km stretch of their flight. Further, Bigg and Turvey then placed their particle counter on Heron Island at the southern end of the GBR from October 1976 to February 1977. During the first month, they observed approximate doublings of particle concentration as the tide was rising. This trend then disappeared with diminishing particle numbers from mid-November. The authors speculated that the correlation of particle concentration with tide was consistent with the explanation that exposed algae and coral emitted DMS that eventually led to particle production. Recent studies have confirmed that the GBR is a significant source of DMS emissions (Jones and Trevena, 2005 and references therein). However, there is still no direct evidence of new particle formation from the GBR, let alone evidence of sulphate- or iodine-mediated nucleation.

2.2.8 Marine aerosol summary

Section 2.2 of this review has discussed the current state of knowledge regarding marine aerosols. The number concentration of marine aerosol particles is relatively stable and generally in the range 200–800 cm^{-3}. The majority of these particles have diameters between ~20–600 nm and they congregate in two dominant modes: the Aitken and accumulation modes. These modes are separated by a minimum in particle number size distribution at around 80 nm, which results from repeated in-cloud processing cycles.

Stable particle number concentration in the face of continuous wet and dry deposition implies there are consistent sources of new MBL particles. The dominant natural sources appear to be the entrainment of freshly nucleated particles from the FT, which are predominantly nss-sulphates, and the bubble-mediated production of sea spray particles. The relative importance of these sources (and particle types) depends on atmospheric conditions such as FT entrainment rate and wind speed over the ocean surface. Once formed, marine aerosols can grow by gaining DMS-derived nss-sulphate mass through condensation and cloud processing. Thus it appears likely that a significant fraction of marine aerosol will be internally mixed nss-sulphate, sea salt and ocean-derived primary organic material. In addition, marine aerosols may also contain a secondary organic component derived from biogenic volatile organic vapours such as DMS, isoprene and monoterpenes.

Very rarely in the remote MBL, a nucleation mode ($3 \leq d_p \leq 25$ nm) also appears in size distributions following the formation of new atmospheric particles. Coastal environments on the other hand, appear to frequently support such particles. At Mace Head, Ireland and Roscoff, France coastal particle production has been linked to iodine-containing gases emitted from exposed macroalgae at low tide. It remains to be seen whether this mechanism of particle formation also occurs at other coastal sites and over the open ocean.

2.3 Water uptake by aerosol particles

2.3.1 Introduction

Water uptake refers to the ability of an aerosol particle to take up water from the surrounding atmosphere. This can occur when the atmosphere is both subsaturated (RH < 100%) and supersaturated (RH > 100%) with respect to water vapour. Water uptake under subsaturated conditions is referred to as hygroscopic growth. Hygroscopicity determines the size and phase of an aerosol particle at a given RH. This in turn determines its radiative properties and the chemical reactions it is involved in. Therefore, it is important to accurately characterise the hygroscopic properties of different aerosol systems in order to correctly model the direct effects of aerosols on climate and important atmospheric chemical processes.

Water uptake by aerosol particles under supersaturated conditions is termed cloud condensation nuclei (CCN) activation because it is the process by which aerosol particles can increase dramatically in size (up to 1000x original diameter) to form cloud droplets. Supersaturated conditions in the atmosphere primarily occur in rising, adiabatically expanding air masses. The microphysical properties of clouds (e.g. cloud droplet number, cloud droplet effective radius) are heavily influenced by the updraught velocities of these rising air parcels. However, they are also influenced by the size distribution and chemical composition of the aerosol particles acting as CCN. For example, if underlying aerosol composition changes causing an increase in CCN concentration for a fixed cloud water content, it will lead to an increase in cloud droplet concentration and corresponding decrease in cloud droplet effective radius (as there is less water vapour available per droplet). The cloud will contain a larger number of smaller droplets which will increase its albedo (the ratio of reflected to incident light) (Twomey, 1974). Therefore, it is important to investigate the ability of aerosol particles to take up water under supersaturated conditions (their ability to act as CCN) in order to elucidate the indirect, cloud-related effects of aerosols on climate.

This PhD research program involved field measurements of the hygroscopic properties of marine aerosol particles. It did not include any direct measurements of water uptake of marine aerosols under supersaturated conditions (i.e. CCN measurements). However, the results of the hygroscopicity measurements have implications for the ability of the investigated particles to act as CCN. Therefore, the concepts behind aerosol water uptake under both sub- and supersaturated conditions are discussed in this literature review.

2.3.2 Important water uptake concepts

Particles can be either hygroscopic, which means they will readily take up water vapour and increase in size, or non-hygroscopic (or hydrophobic), which means they won’t. Hygroscopic growth is most intuitively quantified by a diameter (or mass) hygroscopic growth factor (*HGF*), which is simply the ratio of wet particle diameter at a given RH to dry particle diameter. Non-hygroscopic aerosols have a *HGF* of 1.

The response of a particle to changes in humidity depends on its size and chemical composition, an example is shown for 97 nm ammonium sulphate particles in Fig. 2.1. Some pure substances (e.g. inorganic salts such as ammonium sulphate and sodium chloride) are known to exhibit deliquescence behaviour. This means they will not begin taking up water as ambient RH is increased until a specific threshold is reached. This is known as the *Deliquescence Relativity Humidity* (*DRH*) for that salt. For example, 97 nm ammonium sulphate particles have a *DRH* of 80% (Fig. 2.1). Physically, the *DRH* corresponds to the RH required for enough of the salt to become dissolved in the surrounding water vapour so that it is thermodynamically more stable for the salt to be in an aqueous rather than solid state. Practically, deliquescence is indicated by a sudden increase in the diameter *HGF* of a particle due to water uptake (Fig. 2.1). Above deliquescence an aerosol droplet will take up water much more readily with increasing RH as it seeks to maintain equilibrium between the ambient water concentration and the water vapour pressure just above its surface.

Once a salt particle has deliquesced, it generally won't re-crystallise if the ambient RH is then decreased moderately below its *DRH*. Even though it is thermodynamically more stable for the salt to be in its solid state, it remains in the aqueous phase as a supersaturated solution droplet until enough water has evaporated to support rapid homogeneous nucleation of crystals in the droplet. This doesn't usually occur until the ambient RH is much lower than the *DRH*, at a threshold value known as the *Efflorescence Relative Humidity* (*ERH*). For example, 97 nm ammonium sulphate particles have an *ERH* of 32% (Fig. 2.1). The mismatch of *DRH* and *ERH* for a given salt is classified as a hysteresis phenomenon. It implies that the phase of a salt particle cannot be known simply from the ambient RH when it is between *DRH* and *ERH*; it is also necessary to know the RH history of the particle (i.e. whether is it being hydrated or dehydrated).

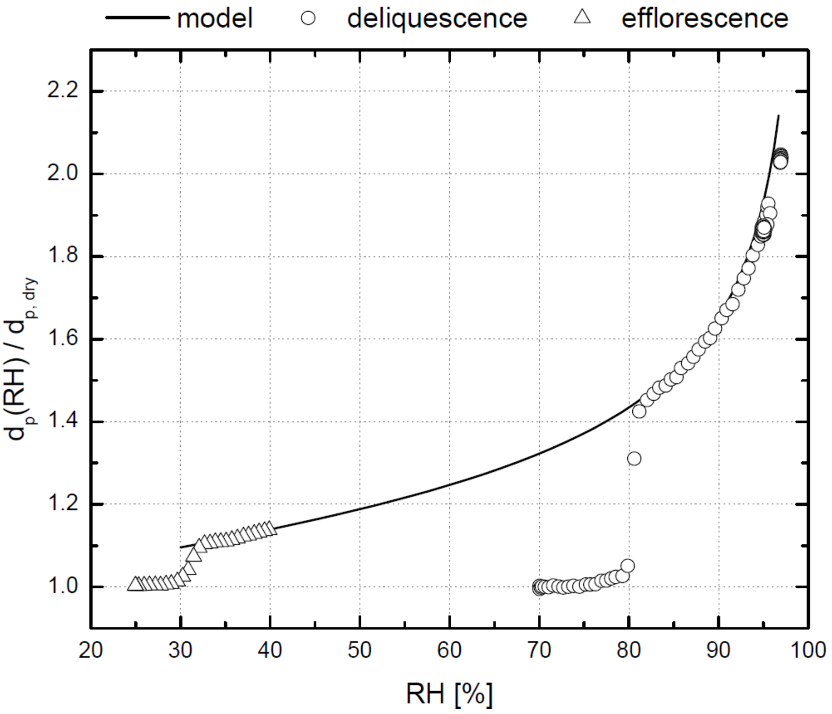


Figure 2.1: Deliquescence and efflorescence curves for 97 nm ammonium sulphate particles (measured by the author and A/Prof Zoran Ristovski at the ILAQH, QUT).

It is important to note that some atmospherically relevant substances don't exhibit deliquescence behaviour. For example, sulphuric acid (H_2SO_4) particles are associated with some water even at very low RH values. Such substances exhibit smooth, continuous and reversible hygroscopic growth with increasing RH. There are also substances, such as water insoluble organic species, that are non-hygroscopic and won't take up any water at RH below 100%.

Once a substance has deliquesced and formed an aqueous solution droplet, the equilibrium between the water activity of that solution (a_w) and water vapour in the surrounding atmosphere is described by the Köhler equation (Seinfeld and Pandis, 1998):

$$\frac{RH}{100} = S = a_w \exp\left(\frac{4\sigma V_w}{RTd_p}\right) \qquad \text{.../Eq. 1}$$

Where S is water saturation ratio, σ is the surface tension of the solution, V_w is the partial molar volume of water in solution, R is the universal gas constant, T is temperature and d_p is droplet diameter. The partial molar volume of water in solution, V_w, is commonly approximated by the molar volume of pure water, which is equal to the molecular weight of water divided by its density (MW_w/ρ_w) (Kreidenweis et al., 2005).

The Köhler equation encompasses two competing effects. The Raoult effect, represented by water activity (a_w), tends to decrease the vapour pressure over a solution droplet, while the Kelvin effect, represented by the exponential term in Eq. 1, tends to increase it. The action behind the Raoult effect is an increase in solute concentration with decreasing droplet diameter (for a constant solute mass). This causes a decrease in the water activity of the droplet and therefore a decrease in the vapour pressure above its surface. For this reason the Raoult effect is also commonly known as the solute effect. The principle behind the Kelvin effect is the fact that the saturation vapour pressure required to maintain vapour-liquid equilibrium is greater over a curved surface than it is over a flat surface. This results in a tendency for vapour pressure to increase as droplet diameter is reduced and solution curvature increases. The Kelvin effect is only significant for particles with initial diameters less than ~100 nm. Above this, the exponential term in the Köhler equation approaches unity and the water activity of a solution droplet simply equates to ambient RH. The competing actions of the Raoult and Kelvin effects and the resulting Köhler curve are displayed in Fig. 2.2 for a 100 nm dry diameter ammonium sulphate particle. There is a maximum in the Köhler curve at the point separating the regions where the Raoult effect is dominant (small, highly concentrated droplets) and where it is insignificant (large, dilute droplets) and therefore the Kelvin term dominates, even if it is only slightly greater than 1.

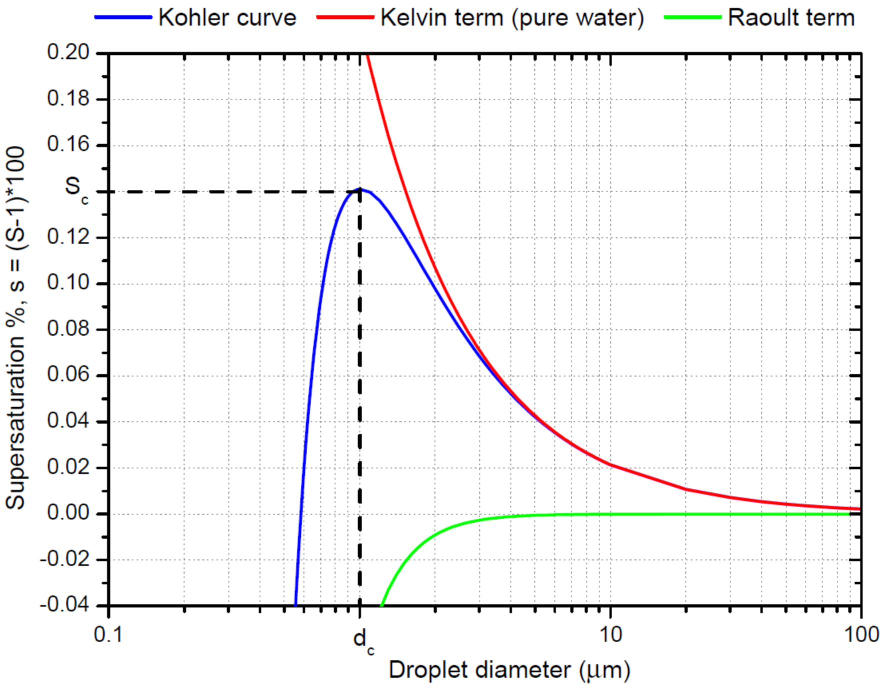


Figure 2.2: The Köhler curve of a 100 nm dry diameter ammonium sulphate particle. The Kelvin and Raoult terms are displayed separately to illustrate their competing actions. S_c is the critical supersaturation ratio and d_c the corresponding critical diameter for the particle.

The position of the Köhler curve maximum is a unique function of a particle's chemical composition and dry diameter. It occurs at a critical supersaturation value, S_c, which is associated with a critical droplet diameter, d_c, as indicated in Fig. 2.2. If the ambient saturation ratio is less than the critical supersaturation ($S<S_c$) for a given particle, it will be in a stable equilibrium with its surroundings at a diameter smaller than its critical diameter. Once the ambient saturation ratio exceeds the critical ratio for a given particle ($S>S_c$), as may occur in a rising air parcel, there is no longer a stable equilibrium size for that particle. Water will continually condense onto the particle increasing its diameter for as long as the ambient saturation ratio is greater than the critical value. This is known as CCN activation (Seinfeld and Pandis, 1998). In a real cloud formation scenario the growth of a cloud droplet is limited by the total supply of water vapour that must be shared between all droplets in the cloud.

2.3.3 Measuring water uptake

Hygroscopic growth

It is possible to accurately measure the water uptake of aerosol particles in both the subsaturated (hygroscopic growth) and supersaturated regimes. The most common instruments used to investigate hygroscopic growth are the Hygroscopic Tandem Differential Mobility Analyser (HTDMA) (Liu et al., 1978; Rader and McMurry, 1986) and the electrodynamic balance (EDB) (Davis et al., 1990). The principle behind both of these instruments is to humidify a single particle (EDB) or ensemble of particles (HTDMA) at a precisely controlled RH before measuring the change in particle size (HTDMA) or mass (EDB) relative to a dry reference point. There are also less rarely used methods that measure change in particle properties upon humidification using principles other than differential mobility analysis or electrodynamic balance (e.g. optical particle counter, Hegg et al., 2007; Stratmann et al., 2004: nephelometer, Fierz-Schmidhauser et al., 2010). In addition, spectroscopic techniques such as Fourier Transform Infra-Red (FTIR) spectroscopy (Braban et al., 2003) can be used to identify water in aerosol particles and study phase transitions directly. Hygroscopic growth can also be studied with RH-controlled environmental cells in optical (Parsons et al., 2004), scanning electron (Ebert et al., 2002) or transmission electron (Wise et al., 2005) microscopy. These methods have the advantage of being able to observe morphological changes during water uptake.

Many of the above techniques are only capable of measuring super-micrometre aerosols and/or are limited to highly controlled laboratory studies (e.g. EDB, FTIR, microscopy). These are advantageous for very precise water uptake measurements. For example, the EDB obtains accurate water activity data suitable for use in thermodynamic models (e.g. Peng et al., 2001a; Tang and Munkelwitz, 1994). These large particle and/or lab based approaches are complemented by the HTDMA, which is capable of measuring small particles (from 6 nm to a few hundred nm in diameter) and can be easily employed in both laboratory and field situations. A modified HTDMA was used to obtain the measurements collected as part of this research program so it is the type of instrument that is discussed in most detail here.

The HTDMA is a continuous gas flow system that consists of 2 differential mobility analysers (DMA) separated by a humidity conditioning system. The first DMA is used to extract a monodisperse distribution of particles around a chosen electrical mobility diameter from dried and charged input aerosol. These particles are then brought to a precisely controlled RH value in the humidifier before being classified by the second DMA, which should be at the same RH as the humidifier along its entire length. The voltage of the second DMA can be stepped or scanned and its output measured with a condensation particle counter (CPC) in order to build a size distribution of the humidified particles. This measured size distribution will only be a slightly skewed and smoothed version of the true humidified particle size distribution due to the finite and size-dependant widths of the DMA transfer functions. An appropriate inversion algorithm is necessary to obtain true distributions from measured ones (Gysel et al., 2009). Most HTDMA studies report average *HGFs* calculated from humidified particle size distributions (and selected dry diameter) or the average *HGFs* of modes within those distributions for externally mixed aerosols containing components with different hygroscopic properties. For such externally mixed aerosols it is also common to report the number fraction of particles in the separate hygroscopic modes. Some studies also report the spread of growth factors around the average *HGF* (the width of the hygroscopic modes).

Many different custom-built versions of the HTDMA exist (e.g. Biskos et al., 2006a; Cubison et al., 2005; Hennig et al., 2005; Johnson et al., 2008; Nilsson et al., 2009; Weingartner et al., 2002). These differ mainly in the type of DMAs and CPCs they employ, whether or not they have a pre-humidification option, the techniques they use to regulate DMA sheath flow rates and the techniques they use to achieve, control and measure humidity and temperature (which are intrinsically linked). Six different HTDMAs were recently tested in an inter-comparison workshop (Duplissy et al., 2009). While good agreement was obtained between the different systems when measuring 100 nm ammonium sulphate particles, they did not agree well when measuring chamber-generated secondary organic aerosol (SOA).

Possible sources of error in HTDMA hygroscopic growth measurements include: RH (or temperature) gradients and instability, poorly calibrated DMA sheath flow rates and high voltage (HV) supply, irregularly shaped (non-spherical) particles, incomplete drying of aerosol before the first DMA, large fractions of multiply charge particles and the incorrect assumption of equilibrium between aerosol and surrounding water vapour (i.e. too short humidification time) (Chan and Chan, 2005; Duplissy et al., 2009; Swietlicki et al., 2008). Suitable solutions exist for minimising these errors. Systems placed in actively temperature controlled cabinets (Duplissy et al., 2009) or with fast-response humidity control (Johnson et al., 2008) can achieve high RH stability. DMA sizing (flow rates and HV supply) can be calibrated with polystyrene latex (PSL) spheres of known diameter. Data analysis procedures exist for taking account of irregularly shaped (Biskos et al., 2006c) and multiply charged particles (Gysel et al., 2009) and suitably long residence times (~10 secs) can be used to satisfy the equilibrium assumption (Sjogren et al., 2007). Indeed, error minimisation in well-tuned modern HTDMA systems has proceeded to such a point that measurement error is mainly dictated by the accuracy of hygrometers used to measure RH. These require ambient and dew-point temperature measurements in order to calculate RH. These are accurate to ±0.1°C, which corresponds to an RH error of ±1.1% at 90% RH. This error decreases with decreasing RH. The accuracy of the hygrometer combines with theoretical DMA sizing error (~±1%) to produce an error in HTDMA *HGF* measurements of ~±3% at high RH for hygroscopic salts.

Volatility-Hygroscopicity-TDMA (VH-TDMA)

A number of different variations on the TDMA concept have been developed. These replace the humidity conditioning unit of a HTDMA with, for example, a volatility conditioning unit (VTDMA; Orsini et al., 1999), a flow tube reactor (McMurry et al., 1983) or an alcohol vapour conditioning unit (OTDMA; Joutsensaari et al., 2001). In addition, combined Volatility Hygroscopicity TDMAs have been developed (VH-TDMA) (Johnson et al., 2004; Villani et al., 2008). The first VH-TDMA was developed at QUT (Johnson et al., 2004) and it consists of a differential mobility analyser (DMA) followed by a thermodenuder (volatility conditioner) and then a humidifier. Two more DMAs with CPCs are placed after both the heating and humidification stages to examine any size changes resulting from these conditioning steps. Thus, the QUT VH-TDMA can be thought of as a V-TDMA and VH-TDMA operating in parallel. It is capable of measuring hygroscopic growth factors as a function of both humidity and volatilisation temperature. This allows investigation of the hygroscopic properties of different components in internally mixed particles, from which the effects of organics on water uptake can be judged (Fletcher et al., 2007; Johnson et al., 2005; Meyer et al., 2009; Meyer and Ristovski, 2007; Ristovski et al., 2010; Sellegri et al., 2008; Villani et al., 2009).

In addition, it is possible to make inferences regarding chemical composition from VH-TDMA scans because the volatile and hygroscopic properties of particles are determined by their chemical composition. Single TDMA techniques (e.g. VTDMA or HTDMA) are limited in their ability to infer composition by the fact that different chemical species can display similar physical properties (i.e. volatility and hygroscopicity are non-unique functions of chemical composition). The VH-TDMA addresses this problem by simultaneously measuring the volatile and hygroscopic properties of particles. This combined TDMA approach significantly constrains the list of potential chemical species within atmospheric nanoparticles (Johnson et al., 2005; Modini et al., 2009; Ovadnevaite et al., 2009; Ristovski et al., 2010).

CCN activity

The water uptake behaviour of atmospheric particles under supersaturated conditions is measured with a CCN counter. A range of different CCN counter designs have been proposed (see McFiggans et al., 2006 and McMurry, 2000 for a review of these different designs). However, they all work on the same concept of measuring the concentration of particles that uptake water to form cloud droplets at a given water supersaturation ratio, $s = S-1$ (ranging from ~0.01-1%). The different designs of CCN counters differ in the way they achieve supersaturated conditions, the residence time of the particles in the instrument and the way they measure the concentration of particles that have activated. It is difficult to strictly control water supersaturation ratio and to determine the maximum supersaturation ratio achieved in a given instrument so measurements from different CCN counters are not necessarily comparable (McMurry, 2000). Many CCN counters are able to measure the concentration of activated particles at different, discrete supersaturation ratios to obtain a CCN activation spectrum.

2.3.4 Calculating water uptake

The water uptake of atmospheric aerosols is calculated assuming thermodynamic equilibrium between particles and water vapour in the surrounding air. That is, it is calculated with Köhler theory (Eq. 1). For particles of a given composition, the Köhler equation describes the equilibrium droplet diameter at a given RH (which can be used to calculate *HGF*) and its maximum represents the critical supersaturation ratio required for CCN activation. It needs to be stressed that the traditional Köhler equation (Eq. 1) applies only to completely soluble species. In reality, atmospheric aerosols also contain insoluble and partially soluble components that can potentially form solid and immiscible liquid fractions and partition to varying degrees to the surface of droplets (McFiggans et al., 2006). In addition, the dissolution of surrounding trace gases during droplet growth can affect further water uptake (Kulmala et al., 1993). Therefore, the traditional Köhler equation (Eq. 1) needs to be modified to account for such possibilities. Such modifications have been proposed in the literature (Gorbunov and Hamilton, 1997; Gorbunov et al., 1998; Laaksonen et al., 1998; Shulman et al., 1996). These forms of the Köhler equation can be circumvented to some degree by coupling the traditional Köhler equation (Eq. 1) with direct empirical parameterisations of water activity or thermodynamic equilibrium models that account for partitioning between different phases.

Combined Köhler theory-thermodynamic equilibrium models are the most fundamental technique for calculating water uptake. Specifically, they determine the gas-particle equilibrium of volatile compounds, including water, in an aerosol system for a given chemical composition and ambient conditions. In practice this is achieved by minimising the total Gibbs free energy (*G*) of the system. Gibbs free energy is a function of temperature, pressure and the number of moles and chemical potential of all components in a system. Atmospheric aerosol systems can consist of several chemical components (water, inorganic and organic) in various phases including highly supersaturated aqueous phases (solution droplets). Therefore, the chemical potentials of gases, solids, water and non-ideal solutions (and their activity coefficients) need to be considered in the minimisation of Gibbs free energy. In addition, for aerosols containing a significant fraction of particles below ~100 nm the calculated equilibrium needs to be consistent with the Kelvin effect (Ming and Russell, 2002; Topping et al., 2005a).

Equilibrium models vary in the chemical species they include, the temperature ranges they are applicable over, the techniques they use to achieve Gibbs free energy minimisation and the models they use to calculate solution activity coefficients and water activity (Zhang et al., 2000). The availability of thermodynamic data for inorganic components means that there is a validated model for calculating the solution activity coefficients and water activity of atmospherically relevant pure or mixed inorganic solutions even at the very high concentrations found in supersaturated aerosol droplets (The Pitzer-Simonson-Clegg mole fraction model used in AIM: http://www.aim.env.uea.ac.uk/aim.htm; Clegg et al., 1998a,b; Clegg et al., 1992). The corresponding models for soluble organic solutions are usually predictive activity coefficient models that group similar compounds together to deal with the large range of possible organic compounds. Experimental data may be fitted to obtain activity coefficients for a few compounds in a group, but the fitted parameters are applicable to the whole group. The most widely used predictive model for calculating the solution activities of organic solutions is UNIFAC (Fredenslund et al., 1975).

Efforts have also been made to create equilibrium models for calculating the solution activity coefficients for multi-component solutions that take into account organic-inorganic interactions as well as organic-water and inorganic-water interactions (Clegg et al., 2001; Erdakos et al., 2006; Ming and Russell, 2002;

Raatikainen and Laaksonen, 2005; Zuend et al., 2008). However, the development of these models is restricted by a lack of experimental data on relevant interaction parameters (Tong et al., 2008). This problem is avoided in models that assume a simple additive approach for the water activities of organic and inorganic components in solution (Topping et al., 2005b), although this assumption (a form of the ZSR assumption) is likely to introduce some error into predicted water uptake, particularly at low RH and high solute concentrations.

The scarcity of multi-component solution activity data restricts the range of situations where detailed thermodynamic models can be applied and as input they require compositional data that are lacking for many atmospheric aerosol systems. In addition, these models are complex to build and computationally expensive. In many cases it is more appropriate to use empirical parameterisations in order to efficiently calculate aerosol water uptake. This approach requires measurement of the water activity of aerosol droplets (non-ideal solutions) as a function of their size (solution composition). These data can then be used directly in the traditional Köhler equation to calculate equilibrium sizes (and *HGF*) and CCN activation diameters for that aerosol. Empirical approaches are commonly combined with the Zdanovski-Stokes-Robinson (ZSR) mixing rule (Chen et al., 1973; Stokes and Robinson, 1966), which is derived under the assumption that the components of an internally mixed particle act independently of each other. With ZSR only single component empirical data are needed to predict the water content of an entire mixture.

A number of empirical approaches have utilised HTDMA or CCN (S_c vs. d_p) data to parameterise the water activity of atmospheric particles as a function of their composition represented by hygroscopicity parameters. A few different hygroscopicity parameters have been devised for this purpose. One widely used parameter is the apparent soluble volume fraction, ε, defined as the volume fraction of an appropriately chosen model salt (often ammonium sulphate) in a dry particle consisting of the model salt and an insoluble core and having the same hygroscopic growth as the actual particle (Swietlicki et al., 2008).

The apparent soluble volume fraction can be easily calculated from HTDMA-measured *HGF* data and in such a way so that the influence of the Kelvin effect is removed from the measurement (Swietlicki et al., 1999). In this respect the apparent soluble volume fraction is a better representation of hygroscopicity than *HGF* because it is more closely linked to chemical composition and values for different sized particles can be directly compared. The ε parameter can be combined with appropriate representations of water activity (e.g. van't Hoff (i) or osmotic coefficient (Φ) representations; see Appendix A of Rose et al., 2008) for the chosen model salt in order to investigate the CCN activity of atmospheric aerosols with Köhler theory (Hameri et al., 2001; Mertes et al., 2005; Rissler et al., 2004; Svenningsson et al., 1994; Svenningsson et al., 1992). The main problem with the parameter is that it is associated with a choice of model salt and it can give rise to the erroneous interpretation that it is the actual soluble volume fraction for an aerosol and that 1- ε is therefore its insoluble volume fraction.

To sidestep this possible misinterpretation single-parameter representations of hygroscopicity have recently been developed that incorporate the composition dependant parameters that tie ε to a choice of model salt (Petters and Kreidenweis, 2007; Rissler et al., 2006; Wex et al., 2007). Of these the Petters and Kreidenweis kappa parameter (κ) appears to be catching on most widely, although it should be noted that a similar parameter was first introduced in the Rissler paper and coincidentally also denoted as kappa. Petters and Kreidenweis define the kappa parameter (κ) as an expression of water activity on a volume basis such that under the ZSR assumption the Köhler equilibrium for a multi-component aerosol droplet can be described as:

$$S = \frac{d_p^3 - d_{dry}^3}{d_p^3 - d_{dry}^3(1-\kappa)} \cdot \exp\left(\frac{4\sigma V_w}{RTd_p}\right) \qquad \text{…/Eq. 2}$$

Where the Kelvin parameters are the same as those described for Eq. 1 and total κ parameter for the droplet is given as:

$$\kappa = \sum_i \varepsilon_i \kappa_i \qquad \text{…/Eq. 3}$$

Where ε_i is the volume fraction of component i and κ_i is its hygroscopicity parameter. These equations are known as κ-Köhler theory.

Physically, kappa represents the volume of water that is associated with a unit volume of dry particle. It can range from 0 for non-hygroscopic (but wettable) species to ~1.3 for very hygroscopic species (e.g. $\kappa_{NaCl} = 1.28$). The majority of atmospheric particles have kappa between 0.1 and 0.9 (Petters and Kreidenweis, 2007). Kappa is a good representation of hygroscopicity because it is independent of the Kelvin effect (like ε but unlike *HGF*), it is not linked to a model salt (unlike ε) and its formulation provides an explicit link between sub- and super-saturated water uptake. In addition, its mixing rule (Eq. 3) means it can be applied to multi-component particles containing water soluble and insoluble ($\kappa = 0$) species. A more general form of κ-Köhler theory has also been derived to account for limited solubility components (Petters and Kreidenweis, 2008).

Regardless of whether rigorous thermodynamic models or empirical parameterisations (ε, κ) are used to calculate water activity, any Köhler model of water uptake that includes treatment of droplet curvature also needs to consider how the Kelvin term in Eq. 1 and its parameters (surface tension, partial molar volume of water) depend on aerosol composition. It has been shown that approximating the partial molar volume of water with the molar volume of pure water (molecular weight of water divided by the density of water (MW_w/ρ_w)) for common inorganic aerosol species introduces insignificant errors into the prediction of equilibrium diameter at a given RH (Brechtel and Kreidenweis, 2000). However, these errors increase with decreasing RH (increasing solute concentration) and they may be important for highly concentrated metastable droplets.

The treatment of droplet surface tension is more difficult. In general, inorganic species have only a minor influence on surface tension but organics can reduce it significantly (Dinar et al., 2006; Facchini et al., 2000; Facchini et al., 1999; Kiss et al., 2005). A reduction in surface tension will result in a decrease in the Kelvin factor. However, this is only significant for water uptake when the Kelvin effect is either comparable to or dominates the Raoult effect. This means surface tension effects are important at high RH or supersaturated conditions and at small dry particle diameters (Hämeri et al., 2000; Topping et al., 2005a,b). For example, at RHs below ~95% changes in surface tension have an insignificant effect on equilibrium droplet diameters for particles greater than 50 nm (Wex et al., 2008). Therefore, surface tension is frequently ignored in calculations of hygroscopic growth by simply assuming it is equal to the surface tension of water. Such an assumption cannot be made in the supersaturated regime for organic-containing aerosols and accurate models or mixing rules to calculate multi-component surface tension as a function of composition are necessary to prevent over-prediction of critical supersaturation (Topping et al., 2007). However, these models need to also consider the tendency of surface active molecules to partition to the surface of solution droplets so that their negative influence on the Raoult effect (solute concentration) as well as the Kelvin factor (surface tension) is properly captured and under-prediction of critical supersaturation is avoided (Kokkola et al., 2006; Sorjamaa and Laaksonen, 2006; Sorjamaa et al., 2004; Topping et al., 2007).

It should also be pointed out that surface tension effects have implications for the ability to predict CCN activity from HTDMA-derived hygroscopicity parameters (e.g. κ-Köhler theory) (Wex et al., 2008). Generally these parameters are derived using, for example, Eq. 2 with surface tension equal to the surface tension of pure water. However they are usually derived from *HGF* measurements over a range (80–95% RH) where hygroscopic growth is insensitive to surface tension. Therefore, the effects of changes in surface tension with droplet size (composition) are not picked up by the ‘catch-all’ hygroscopicity parameter. If the derived parameter is then extrapolated and applied in a region where the influence of the surface tension is significant (i.e. RH > 100%) then predicted critical supersaturation points will be wrong unless an appropriate surface tension parameterisation (including partitioning effects) is used. It is worth repeating that this will only occur for aerosols containing components that significantly influence surface tension.

2.3.5 Water uptake by organic-containing aerosols

Until recently it was assumed that organic aerosols were mainly water insoluble and therefore could be neglected in calculations of water uptake by atmospheric aerosols. Over a decade of research has shown that this assumption is too simplistic. For example, a number of closure studies have found that the water content of aerosol samples (particular aged ones) cannot always be explained by their inorganic fraction alone (Dick et al., 2000; Gysel et al., 2004; Saxena et al., 1995; Swietlicki et al., 1999). It is now recognised that organic substances can significantly affect both the hygroscopic growth and CCN activity of atmospheric aerosols.

Hygroscopic growth

The hygroscopic properties of a range of organic aerosols have been studied both experimentally and with thermodynamic models (Ming and Russell, 2001; Topping et al., 2005b). The experimental studies are thoroughly reviewed in section 7 of Kanakidou et al. (2005) and an updated list of references is provided here. Classes of organic compounds that have been investigated either on their own or in mixtures with common inorganic substances include organic acids (Andrews and Larson, 1993; Brooks et al., 2002; Choi and Chan, 2002; Cruz and Pandis, 2000; Hameri et al., 2002; Koehler et al., 2006; Marcolli et al., 2004; Peng et al., 2001a; Pope et al., 2010; Prenni et al., 2003; Prenni et al., 2001; Svenningsson et al., 2006; Wise et al., 2003), atmospheric humic-like substances (HULIS[3]) (Badger et al., 2006; Brooks et al., 2004; Chan and Chan, 2003; Gysel et al., 2004; Hatch et al., 2009; Svenningsson et al., 2006; Wex et al., 2007; Ziese et al., 2008), sugars (Koehler et al., 2006; Peng et al., 2001b; Svenningsson et al., 2006), proteins (Mikhailov et al., 2004), organic salts (Gysel et al., 2004; Peng and Chan, 2001), pharmaceuticals (Chan et al., 1997; Peng et al., 2000) and chamber-generated SOA (Baltensperger et al., 2005; Good et al., 2010; Juranyi et

---

[3] A general term for macromolecular, multifunctional, polyacidic organic compounds that are ubiquitous in atmospheric aerosols (e.g. Graber, E. R., and Rudich, Y.: Atmos. Chem. Phys., 6(3), 729-753, 2006).

al., 2009; Meyer et al., 2009; Takahama et al., 2007; Varutbangkul et al., 2006; Wex et al., 2009).

Many of these organic substances display significant hygroscopic growth at RH values below 100%, although they still do not grow as much as common inorganic aerosol species such as ammonium sulphate and sodium chloride. For example, at 90% RH dicarboxylic acids have diameter *HGFs* in the range ~1–1.4, although $HGF_{90\%}$ as high as 1.73 has been measured for 100 nm malonic acid particles (Prenni et al., 2001). Chamber-generated SOA has $HGF_{90\%}$ of ~1.1–1.4 and HULIS particles have $HGF_{90\%}$ in the range ~1.03–1.5. In terms of kappa (κ), organics have values in the range ~0.01–0.4, where the upper limit is set by malonic acid (Petters and Kreidenweis, 2007). Relatively water soluble organic compounds can cause significant reductions in the deliquescence relative humidity's (*DRHs*) of mixed organic-inorganic particles compared to the *DRHs* of inorganic species on their own. Slightly water soluble or insoluble organic species do not have this depressing effect on *DRH*. At higher RHs, the hygroscopic growth factors of mixed organic-inorganic particles are lower than what would be expected for the inorganic components alone because, in general, soluble organics are less hygroscopic than inorganic aerosols above deliquescence and some organics may still be insoluble and therefore hygroscopically inactive even at high RH.

The depression of the *DRH* of an inorganic salt when mixed with a soluble organic component is an important result. It can be shown theoretically that the *DRH* of a multi-component particle is lower than the *DRHs* of the individual components it is made of (Seinfeld and Pandis, 1998). This concept has been extended experimentally to internally mixed organic-inorganic particles (Marcolli et al., 2004). This study was able to confirm that the *DRH* of dicarboxylic acid solutions decrease with increasing number of organic compounds (up to 5) in solution. A further decrease in *DRH* was observed when an inorganic salt (NaCl) was added to the dicarboxylic acid mixture. This suggests a liquid phase will always be present in atmospheric aerosols because they frequently exhibit a high degree of internal mixing.

CCN activity[4]

Organic compounds can also affect the water uptake of atmospheric particles in the supersaturated regime. The different and often contradictory mechanisms by which they exert this influence thermodynamically can be understood keeping in mind the theoretical discussion of Köhler theory in the previous section (2.3.4). Firstly, organic species can alter the equilibrium between the size of a particle and its surrounding water vapour concentration through the Raoult term in the Köhler equation (Eq. 1). Some organic compounds are only partially soluble or even completely insoluble in water. Their presence reduces the amount of dissolved material in aerosol droplets, which decreases the droplet diameters at which the Raoult effect becomes significant for a given dry particle mass and increases the critical supersaturation ratios required for CCN activation. Some organic species are too insoluble to ever activate at realistic atmospheric supersaturations. Remarkably, this was already noted by John Aitken in 1880 who observed that although camphor evaporated substantially into the atmosphere when heated, water vapour hardly condensed onto the resulting aerosol to form fog unlike it did for salt aerosols (Aitken, 1880). For a given aerosol population, limited solubility organic components tend to decrease the number of particles available as CCN.

However, experimental studies have shown that the critical supersaturation ratios of mixed slightly soluble organic-inorganic particles are strongly dependent on initial particle phase. Initially solid particles that still contain an insoluble, solid inclusion activate at high critical supersaturation ratios according to modified forms of the Köhler equation (Laaksonen et al., 1998; Shulman et al., 1996). However, initially liquid particles of the same composition activate at lower critical supersaturation ratios and behave as if all substances were completely soluble as described by the traditional Köhler equation (Eq. 1) (Bilde and Svenningsson, 2004; Henning et al., 2005; Hori et al., 2003). In addition,

---

[4] The concepts raised in this discussion apply equally to water uptake in the subsaturated regime, although it should be kept in mind that generally for RH<~95% compositional effects on the Raoult term dominate those on the Kelvin term (e.g surface tension reduction).

experiments have shown that small amounts of inorganic salts internally mixed with poorly soluble organic particles are enough to counteract the limited solubility effect and decrease the critical supersaturation ratio of the mixed particles, even though they are predominantly organic (Bilde and Svenningsson, 2004; Broekhuizen et al., 2004). Real atmospheric particles are likely to be complex mixtures that contain at least some dissolved material, especially after cloud processing. It has also been established that internally mixed organic particles are likely to be in the liquid phase even at low RH (Marcolli et al., 2004). Therefore, it is generally thought that organics with limited solubility will not significantly reduce the concentration of real atmospheric particles that are able to act as CCN (McFiggans et al., 2006).

Secondly, organic species can alter the equilibrium described by the Köhler equation through the composition-dependent parameters in the Kelvin term of the Köhler equation (exponential term of Eq. 1); namely, through droplet surface tension and partial molar volume of water. Most importantly, many organic species are good surfactants and they can significantly reduce the surface tension of aerosol droplets. For example, 1 g L^{-1} solutions of atmospheric HULIS have measured surface tensions 14–42% below the surface tension of pure water (72.8 mN m^{-1}) (Dinar et al., 2006; Kiss et al., 2005). In addition, the surface tension of atmospheric aerosol water extracts and cloud and fog water samples has been observed to decrease significantly with increasing organic content (Facchini et al., 2000; Facchini et al., 1999). A reduction in droplet surface tension causes a decrease in the Kelvin factor, which tends to decrease the critical supersaturation ratio required for CCN activation (Shulman et al., 1996). This is opposite to the effect caused by organic components of limited solubility. For a given aerosol population this tends to increase the number of particles available as CCN, which could potentially increase the reflectivity of any cloud that forms on the aerosol (Facchini et al., 1999; Mircea et al., 2002).

However, organic surfactants do not just influence the Kelvin term in the Köhler equation; they also have a solute-related effect. This is because, by definition, surfactants partition to some degree to the surface of solutions. For aerosol droplets with high surface-to-volume ratios this can result in significant reductions in the amount of dissolved material in the bulk of solution droplets. Therefore, not taking surface partitioning into account can lead to under-prediction of critical supersaturation ratios (Kokkola et al., 2006; Sorjamaa and Laaksonen, 2006; Sorjamaa et al., 2004; Topping et al., 2007). This helps to explain, for example, the results of Abbatt and co-workers who observed no changes in CCN behaviour that could be attributed to a reduction in surface tension in droplets containing highly surface active organic acids (Abbatt et al., 2005).

Köhler theory is useful for isolating the thermodynamic effects that organic compounds have on CCN activity but it is unable to explain how these effects will be translated into real atmospheric situations. For this purpose dynamic cloud models that simulate the supersaturated conditions experienced by a distribution of particles in an adiabatically rising air mass are required. For example, Ervens et al. used a cloud parcel model to show that when considered individually, 3 properties of organic compounds (low solubility, increased molecular weight and surface tension suppression) can have significant effects on eventual cloud droplet concentrations (Ervens et al., 2005). However, when all 3 properties were considered together in their model much smaller changes in cloud droplet concentration were observed as the different effects tended to counteract each other.

The above discussion highlights the complex and often contradictory ways that organic compounds can alter the thermodynamic equilibrium between the size of a particle and its surrounding water vapour concentration. This has important and well documented effects on the hygroscopic growth of mixed organic-inorganic particles, which are mainly driven by changes in the amount of dissolved material in aerosol droplets. In the supersaturated regime, the overall consensus of the literature seems to be that although certain properties (surface tension, limited solubility) of organics can individually influence the CCN activity of aerosols, when taken together they counteract each other to an extent and do not exert a significant influence. This could explain why some studies have found size to be an adequate predictor of CCN concentration without having to invoke compositional data (Dusek et al., 2006).

2.3.6 Organic aerosols and the kinetics of water uptake

As well as altering the equilibrium between aerosol particles and surrounding water vapour, organics can also influence the time it takes for particles to reach this equilibrium. These are so called kinetic or mass transfer effects and they are potentially very important in the cloud formation process. They can arise, for example, when organic compounds form films or solid barriers around aerosol particles that inhibit the transfer of water vapour between the soluble interiors of particles and their surroundings.

Numerous examples of organics that influence aerosol water uptake kinetics can be found in the literature. Early reports suggested that organic coatings effectively slowed the evaporation rate of liquid water droplets (Snead and Zung, 1968) and possibly prevented the condensation of water onto particles to form fog droplets (Bigg et al., 1969). More recently, Abbatt et al. observed the complete deactivation of ammonium sulphate particles with thick stearic acid coatings in CCN measurements (Abbatt et al., 2005). This suggested that the organic coatings delayed the condensational growth of the ammonium sulphate cores so the time required for activation was greater than the residence time of the particles in their instrument (~20s).

A few hygroscopic studies have also provided evidence that organic compounds can retard water uptake. For example, Xiong et al. discovered that an organic monolayer inhibited the hygroscopic growth of underlying H_2SO_4 particles (Xiong et al., 1998). Sjogren et al. found an increased equilibrium time for ammonium sulphate particles mixed with either adipic acid or Aldrich humic acid sodium salt. They calculated that growth factors measured with a humidification time of 4secs were up to 7% below growth factors measured at equilibrium (Sjogren et al., 2007). Peng et al. reported that glutaric acid particles took a very long time (~10hrs) to completely deliquesce in an EDB (Peng et al., 2001a) and Chan and Chan also used an EDB to show that thick octanoic acid coatings could delay the hygroscopic growth of coated ammonium sulphate particles (Chan and Chan, 2007). It is important to note that in the experiments capable of measuring final particle size the equilibrium sizes of the particles were all eventually reached in the studies described above.

Observations of real atmospheric particles displaying delayed water uptake are rarer. Chuang employed a novel, modified TDMA arrangement in Mexico City to measure the time required for real atmospheric particles to grow hygroscopically when taken from RH~10% to RH~93% (Chuang, 2003). He discovered that 0–2% of the particles he measured required more than 2–3 secs to grow to their equilibrium size. Johnson et al. used a VH-TDMA (see section 2.3.3) to observe increases in the hygroscopic growth factors of marine particles in nucleation, Aitken and accumulation modes following the removal of volatile organic species (Johnson et al., 2005). The authors calculated that the changes in *HGF* were so large they could only be explained by an increase in the absolute amount of water uptake by the non-volatile particle residuals, and not merely an increase in their hygroscopicity. This indicates that there was a real suppression of water uptake by the organic components on the timescale of humidification in the VH-TDMA system employed in that study (5-10s). Finally in the supersaturated regime, three recent field studies have observed delayed CCN activation of organic-containing particles relative to ammonium sulphate particles (Ruehl et al., 2008, 2009; Shantz et al., 2010).

One possible explanation for all of these observations is that organics were present as a film that slowed the rate of water uptake. It is well established that organic compounds can form films on flat liquid solutions that inhibit the rate of water transfer across the air-liquid interface (Barnes, 1986). For decades researchers have also postulated that atmospheric particles may contain similar organic films (Chuang, 2003; Donaldson and Vaida, 2006; Gill et al., 1983) and recent studies have provided more direct evidence of these (Mochida et al., 2002; Peterson and Tyler, 2002; Russell et al., 2002; Tervahattu et al., 2002; Tervahattu et al., 2005).

Amphiphilic compounds are likely to be the best film-forming compounds because they consist of a hydrophilic polar head and a hydrophobic tail (e.g. long-chain carboxylic acids). The resulting insolubility causes these compounds to congregate at air-water interfaces with their heads pointing into solution and their tails exposed to the air. Depending on surface area per molecule, these films can exist in expanded (gaseous or liquid-expanded) or condensed states. Organic molecules with long, straight carbon chains are favoured to form condensed films because they can pack closely together. On the other hand, bent molecules and complex mixtures of different molecules are less likely to pack closely together and may only be capable of forming expanded films. Soluble compounds (e.g. ethanol) are also capable of forming organic films. In this case the film refers to the spontaneous, preferential partitioning of soluble compounds to the surface compared to the bulk solution. It is thought that only insoluble condensed organic films are capable of significantly impeding water vapour transport (Donaldson and Vaida, 2006; Gill et al., 1983).

While organic films on atmospheric particles appear to be likely it is questionable whether these will be of the condensed, water-inhibiting variety. Firstly, all types of atmospheric environments support complex mixtures of organic aerosols whose molecules are unlikely to pack together tightly. Also, Seidl has combined modelling techniques with measured fatty acid concentrations to show that these organics would generally form open, expanded films on atmospheric particles, although concentrations were high enough at one continental site in the Western USA to suggest fatty acid condensed film formation was possible (Seidl, 2000). However, this study was limited to only one class of organic compounds. A similar analysis needs to be extended to all types of atmospheric film-forming compounds to really investigate whether closed, condensed films are likely to exist.

The degree to which organic films impede the rate of water vapour transfer can be quantified by the mass accommodation coefficient (α), defined as the probability that a colliding water vapour molecule will cross the air-liquid interface of a solution. Despite decades of study the mass accommodation coefficient for water vapour molecules impinging on liquid water is still a contentious figure and results vary from ~10^{-2} to 1. Laaksonen et al. suggested that a mass accommodation coefficient of the order of 1 should be used in cloud models to replicate the observed growth rates of droplets in laboratory studies (Laaksonen et al., 2005). However, organic films can considerably reduce the mass accommodation coefficient of a solution. Chuang reviewed a range of laboratory studies on the evaporation and condensation rates of water vapour from flat and curved solutions with organic films and found mass accommodation coefficient measurements as low as 2×10^{-5} (Chuang, 2003). Furthermore, he estimated that atmospheric particles displaying delayed condensational growth in Mexico City (mentioned above) had accommodation coefficients ranging from $1–4\times10^{-5}$.

The kinetic effects introduced by organic compounds need to be considered in studies of aerosol-cloud interactions as CCN activation time can have a potentially significant effect on resulting cloud properties. This is because particles only experience supersaturated conditions for a finite time interval (~10s–100s of seconds) in adiabatically rising air parcels. Chuang et al. suggested that kinetically limited droplet growth would lead to cloud droplet concentrations smaller than those predicted by Köhler theory (Chuang et al., 1997). This is turn would effect cloud albedo. They suggested that neglecting kinetic effects in calculations of the radiative forcing due to clouds could introduce errors of the same order of magnitude as the radiative forcing due to anthropogenic greenhouse-gases; this is a significant result. Nenes et al. used a cloud parcel model incorporating kinetic effects to show that neglecting them can result in cloud droplet concentrations that are overestimated by up to 40% in urban environments (Nenes et al., 2001). Feingold and Chuang also used a cloud parcel model to show that organic films could potentially reduce cloud droplet concentrations (Feingold and Chuang, 2002). All of these studies highlight why it is necessary to consider the kinetics of water uptake.

2.4 Water uptake by marine aerosols

2.4.1 Introduction

The importance of water uptake by ocean-derived particles was already noted by John Aitken 130 years ago (Aitken, 1880). He concluded Part I of 'On Dust, Fogs and Clouds' with a statement more poetic than most found in scientific literature:

> "The Ocean, which under a tropical sun quietly yields up its waters to be carried away by the passing air, almost looks as if he repented the gift, when tossed and angry under tempestuous winds, as he sends forth his spray, which dried and disguised as fine dust becomes his messenger to cause the waters to cease from their vaporous wanderings, descend in fertilising showers, and again return to their liquid home."

Although it is clear that Aitken qualitatively understood a lot, much more has been learnt about marine aerosols and the way they interact with water vapour in the time since his prescient statement was made. This chapter summarises this knowledge with reference to the previous 2 sections (2.2 and 2.3). It focuses mainly on hygroscopic growth because it is intended primarily as a review of results that can be compared to the VH-TDMA measurements collected in this research program. However, some CCN measurements are also discussed.

2.4.2 Water uptake by particular marine aerosol components

To understand how marine aerosols grow hygroscopically and their potential to act as CCN it is instructive to first examine the water uptake properties of the main species they are composed of. In the case of atmospherically common inorganic species these have been studied extensively in both laboratory (e.g. Tang and Munkelwitz, 1994; Tang et al., 1997) and modelling studies (e.g. Ming and Russell, 2001). As detailed in section 2.2 of this review, the main inorganic marine aerosol species include sulphates (neutralised to varying degrees by ammonia) and sea salts, which are predominantly composed of sodium chloride. Figure 2.3 displays humidograms (*HGF* vs. RH) for these aerosol types. Specifically, curves are plotted for 100 nm spherical particles composed of sulphuric acid (H_2SO_4), ammonium bisulphate (NH_4HSO_4), letovicite

($(NH_4)_3H(SO_4)_2$), ammonium sulphate ($(NH_4)_2SO_4$), sodium chloride (NaCl) and sea salt. These were calculated including consideration of droplet curvature (through Eq. 1) and with water activity, solution density (Tang, 1996; Tang and Munkelwitz, 1994; Tang et al., 1997) and droplet surface tension (Brechtel and Kreidenweis, 2000) parameterisations from the literature. Sea salt particles were assumed to have the surface tension of water and their appreciable hygroscopic growth before deliquescence and after efflorescence was not modelled but estimated from laboratory data for illustrative purposes.

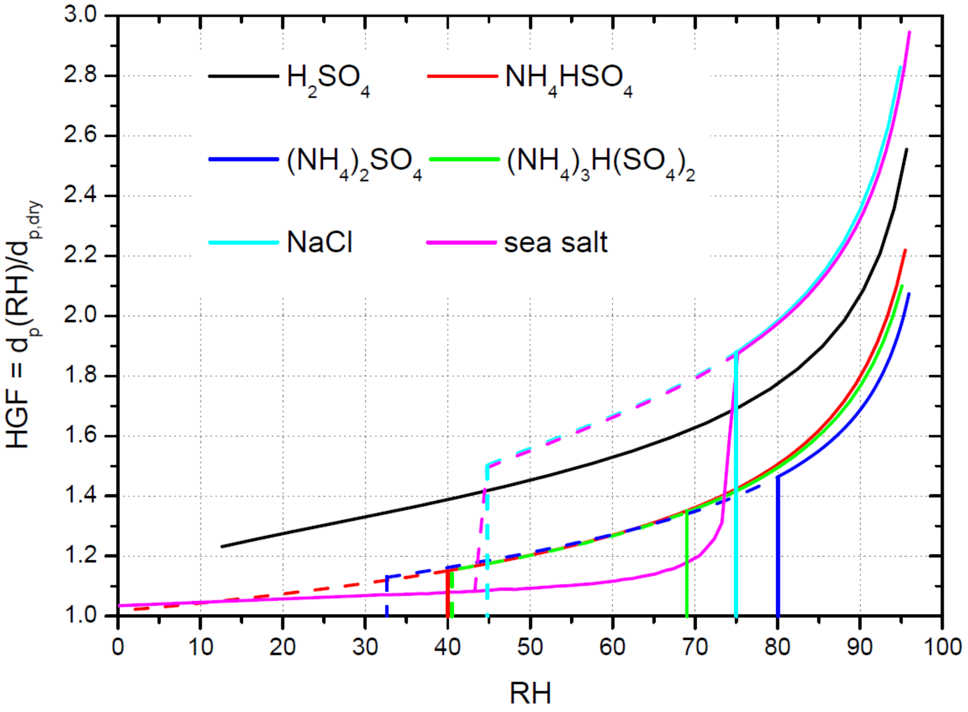


Figure 2.3: Hygroscopic growth factors as a function of RH for 100 nm particles composed of common inorganic components found in marine aerosols. Solid lines indicate hydration branches and deliquescence transitions (i.e. increasing RH) and dashed lines indicate dehydration branches and efflorescence transitions (i.e. decreasing RH).

Sulphuric acid particles display smooth and gradual hygroscopic growth. This is because they are always associated with some water, even at very low RH. On the other hand, more neutralised sulphates such as $(NH_4)_3H(SO_4)_2$ and $(NH_4)_2SO_4$ display clear phase transitions and hysteresis behaviour (i.e. *ERH* < *DRH*) (Biskos et al., 2006b; Tang and Munkelwitz, 1994). This gives rise to 2 branches in their humidograms; one formed as RH is increased (hydration branch, solid lines) and one formed as RH is decreased (dehydration branch, dashed lines). The hygroscopic behaviour of NH_4HSO_4 particles is somewhere in between. Thermodynamically they are expected to deliquesce at 40% RH but experiments have shown that it is difficult to completely dry NH_4HSO_4 particles, even when RH is reduced to 0.05% (Cziczo et al., 1997; Tang and Munkelwitz, 1994). Thus, they probably only ever exist as liquid droplets in the atmosphere and exhibit smooth water uptake, analogous to sulphuric acid particles. At high RHs when all sulphate species have deliquesced, there is a trend of decreasing hygroscopicity with increasing degree of neutralisation. H_2SO_4 particles are considerably more hygroscopic than neutralised sulphates, which all have quite similar *HGFs* but still display the trend.

The situation for sea salt particles is a bit more complicated due to the fact they are composed of a mixture of inorganic salts (see section 2.2.4). NaCl typically comprises over 70% of this mixture on a mass basis. Therefore, the hygroscopic growth of sea salt particles is dictated to a large extent by this component. NaCl particles display abrupt deliquescence at 75% RH and efflorescence at 45% RH. In the liquid state they are very hygroscopic and display *HGFs* much greater than those for sulphates and indeed for all other common atmospheric aerosol species. The principal ionic component that distinguishes the hygroscopic growth of sea salt particles from NaCl particles is Mg^{2+}. This component readily forms hydrated salts in sea salt solutions (e.g $MgCl_2{\cdot}6H_2O$, $MgSO_4{\cdot}H_2O$), which have *DRHs* well below the deliquescence point of NaCl (e.g. $MgCl_2{\cdot}6H_2O$ *DRH* = 33%). This means sea salt particles will always be associated with some water, even at very low RH (Cziczo et al., 1997; Tang et al., 1997). They will also display considerable hygroscopic growth below their full deliquescence point, which occurs at about 74% RH when complete NaCl deliquescence occurs. Therefore, sea salt particles always have *HGF* > 1 unlike pure salts that have *HGF* = 1 below deliquescence and/or efflorescence (Fig. 2.3).

All of the particle types included in Fig. 2.3 display considerable hygroscopic growth above deliquescence. This indicates that they are efficient CCN and measurements confirm this. For example at 0.2% supersaturation, the critical dry diameters required for activation of ammonium sulphate and sodium chloride particles are only 81 nm and 64 nm, respectively. Based on their efficient (and predictable) CCN activation these 2 compounds are frequently used to calibrate CCN counters (Rose et al., 2008).

Marine aerosols can also contain primary and secondary organic components. It is difficult to characterise the water uptake properties of these species simply because there is an enormous range of different organic compounds in the atmosphere, even in relatively clean and simple marine aerosol systems. Nevertheless, the hygroscopic properties of some specific organic species detected in marine aerosols have been investigated. For example, Johnson et al. measured *HGF* at 90% RH of 1.6 for 100 nm methane sulphonic acid (MSA) particles (Johnson et al., 2004). A number of studies have investigated the hygroscopic properties of saccharides, mainly glucose and levoglucosan (Koehler et al., 2006; Peng et al., 2001b; Svenningsson et al., 2006). Saccharides form a major part of primary marine organic aerosols (though not levoglucosan, this is a biomass burning product) (Facchini et al., 2008b; Russell et al., 2010). Glucose and levoglucosan particles both display gradual and continuous hygroscopic growth as a function of RH and 100 nm levoglucosan particles have *HGF* of ~1.3–1.4 at 90% RH (Koehler et al., 2006 and references therein). In regards to supersaturated water uptake, the CCN activation potentials of levoglucosan, glucose and fructose particles are all very similar. At 0.2% supersaturation critical dry diameters in the range 125–137 nm are required for activation (Koehler et al., 2006 and references therein).

A number of investigators have looked at the water uptake properties of dicarboxylic acids (e.g. oxalic, malonic and succinic acid), which have been observed in trace amounts in marine aerosols. Soluble dicaboxylic acid particles (e.g. malonic acid) can display gradual and continuous water uptake while less soluble species (e.g. succinic acid) won’t deliquesce until ~99% RH (Peng et al., 2001a; Prenni et al., 2001). When mixed in equal ratios (not likely in marine aerosols) the soluble species allow NaCl and $(NH_4)_2SO_4$ particles to take up water well below their normal *DRHs* while the insoluble species have no effect

(Choi and Chan, 2002; Prenni et al., 2003). At 90% RH, dicaboxylic acid particles have *HGFs* in the range 1–1.4, although $HGF_{90\%}$ as high as 1.73 has been measured for 100 nm malonic acid particles (Prenni et al., 2001). In regards to supersaturated water uptake, the critical dry diameters required for activation of oxalic acid, malonic acid and succinic acid particles at 0.2% supersaturation are ~80–100 nm, ~90–105 nm and ~90–110 nm, respectively (Koehler et al., 2006; Rissman et al., 2007 and references therein).

Therefore, with the possible exception of malonic acid and MSA, it appears that organic species will have a depressing influence on the hygroscopic growth at high RH and the CCN activation potential of marine aerosols. However, depending on their solubility they may allow marine aerosols to take up water below the deliquescence points of atmospherically common inorganic substances if they are present in large enough quantities.

2.4.3 Water uptake by marine aerosols- laboratory and modelling studies

The organic and inorganic fractions of marine aerosols are likely to exhibit high degrees of internal mixing. Therefore, it is also necessary to take collective approaches when investigating water uptake by marine aerosols. A number of laboratory and modelling studies have done this. Svenningsson et al. atomised solutions of ammonium sulphate (50%), sodium chloride (30%), succinic acid (10%) and fulvic acid (10%) to represent marine aerosol particles in the laboratory (Svenningsson et al., 2006). They found that 100 nm particles produced in this manner did not effloresce above 40% RH, deliquesced at ~65% RH and had *HGF* at 90% RH of ~1.6. Interestingly, this hygroscopic growth was below the growth predicted using the ZSR approximation. This is the assumption that the components of an internally mixed particle uptake water independently of each other. Failure of this assumption could have occurred for a number of reasons pointed out by the authors including the formation of crystals with low solubility or density, the formation of volatile compounds that evaporated during measurement, initially non-spherical particles or organic-inorganic interactions in solution that had a negative effect on water uptake. In the supersaturated regime, the critical dry diameter required for activation of the marine aerosol proxy at 0.2% supersaturation was 80 nm, similar to the value for pure ammonium sulphate.

More attention has been paid to sea spray particles, which are, of course, only a component of the marine aerosol. Investigators have generated sea spray particles by atomising (Niedermeier et al., 2008; Swietlicki et al., 2008) and/or bubbling natural seawater samples (Fuentes et al., 2010; Sellegri et al., 2008; Wise et al., 2009). The results of these studies can be summarised as follows. Sea spray particles do indeed take up significant amounts of water well below the deliquescence point of NaCl, as expected due to the presence of hydrated magnesium salts in the sea salt mixture and possible presence of soluble organic species. Once deliquesced, their hygroscopic growth factors are less than 15% below corresponding NaCl and sea salt growth factors, which again can be explained by the presence of organics (particularly in the Fuentes et al. study, which generated particles from seawater highly enriched in biogenic organics). Related to this, the critical diameters required for CCN activation of sea spray particles can be greater than those required for NaCl particles (Fuentes et al., 2010), although in some cases they are very similar (Niedermeier et al., 2008). It should be noted that these observations are difficult to reconcile with the very large organic fractions (up to 80%) measured for accumulation mode sea spray particles (Facchini et al., 2008b; Keene et al., 2007a). Assuming that sea spray organics are considerably less hygroscopic than sea salt, which is very likely, then such large fractions of organic material would be expected to cause much greater deviations between the water uptake properties of sea spray and sea salt (or NaCl) particles.

The hygroscopic growth of sea spray aerosol has also been investigated from a thermodynamic modelling perspective by Ming and Russell (2001). These authors represented the organic fraction of sea spray particles in their model with 20 insoluble and 4 soluble organic compounds that have been detected in marine aerosols or seawater. The model predictions were broadly in line with what has been observed in the experimental studies. Hygroscopic growth above deliquescence decreased with increasing organic fraction; particles with 30% organic fraction grew 15% less than pure sea salt particles while those composed of equal amounts of organics and inorganics grew 25% less than sea salt particles.

2.4.4 Water uptake by marine aerosols- field studies

Laboratory and modelling studies are useful tools for investigating the water uptake properties of marine aerosols and their components but field measurements are ultimately required to determine these properties under common atmospheric conditions. The majority of hygroscopicity measurements in marine or coastal environments have been taken by HTDMA instruments. These data have been compiled in the form of *HGFs* at 90% RH and discussed in a thorough review of HTDMAs by Swietlicki et al. (2008). The measurements mainly cover particles with diameters in the range 8–250 nm, although particles up to 600 nm have been measured. The data were compiled into 4 categories covering the following $HGF_{90\%}$ ranges for 100 nm dry particles: nearly hydrophobic particles (1.0–1.11), less-hygroscopic particles (1.11–1.33), more-hygroscopic particles (1.33–1.85) and sea salt particles (>1.85). Nearly hydrophobic and less-hygroscopic particles are generally only observed in marine environments in continentally-influenced air masses suggesting they are not ocean-derived. One exceptional region is the Arctic. Here biological fragments (Bigg and Leck, 2008) potentially comprised a less-hygroscopic particle mode which appeared in up to 27% of ship-based HTDMA measurements of nucleation and Aitken mode particles taken during an Arctic summer (Zhou et al., 2001).

More-hygroscopic particles appear in almost 100% of marine HTDMA measurements and thus seem to be ubiquitous in the MBL. Particles in this category have *HGFs* similar to those of ammoniated sulphates, which are known to be a major component of the sub-micrometre marine aerosol. This strongly suggests that the more-hygroscopic particles are predominantly sulphates. Observed growth factors are often greater than those predicted for ammonium sulphate, which could be explained by the fact that many of these particles are only partially neutralised by ammonia resulting in slightly higher growth factors (Fig. 2.3). *HGFs* less than those of ammoniated sulphates are also frequently observed, which might be explained by the presence of internally-mixed organics.

Externally mixed, very hygroscopic sea salt particles (35–350 nm in diameter) only appear at winds speeds greater than ~6 m s^{-1}, consistent with their identification as sea spray particles produced from wind-induced bubbles. However, the Swietlicki et al. review notes that these particles appear far less than would be expected based on wind-speed-dependent sea spray fluxes. The authors suggest that this might be explained by the rapid reaction of sea spray particles with sulphuric acid in the atmosphere, resulting in the partial conversion of sodium chloride to sodium sulphate. 100 nm dry diameter sodium sulphate particles only have $HGF_{90\%}$ of 1.68 (data measured by author with QUT VH-TDMA), so this mechanism might serve to shift particles from the sea salt to the more-hygroscopic particle mode. In addition, sea spray particles potentially contain a large insoluble organic fraction (Facchini et al., 2008b; Keene et al., 2007a) which could also place them in the more-hygroscopic particle mode. Volatility measurements can be used to test both these hypotheses. For example, Tomlinson et al. measured the volatility and hygroscopicity of marine aerosol particles sampled from a ship in the South-eastern Pacific Ocean (Tomlinson et al., 2007). The measured volatilisation temperatures were largely consistent with ammoniated sulphate particles, suggesting that these comprised the observed more-hygroscopic particle mode in this study, not aged or organic-dominated sea spray particles. Thus, it must be said that accumulation mode sea spray particles still remain conspicuous in their absence over the oceans.

Only a handful of studies have examined the hygroscopic growth of marine aerosols as a function of RH (Allan et al., 2009; Berg et al., 1998; Fletcher et al., 2007; Zhou et al., 2001). Most of these measurements have been taken over the RH range ~50–90% although scans from as low as 20% RH were conducted in the Fletcher et al. study. Gradual and continuous water uptake is frequently observed analogous to that of sulphuric acid, incompletely dried ammonium bisulphate or soluble organic particles. However, deliquescence transitions in the range 68–90% RH (Berg et al., 1998) or at ~78.5% (Fletcher et al., 2007) have been observed for smaller particles in Aitken or nucleation modes. These transitions are consistent with more neutralised forms of sulphate (Fig. 2.3) and the fact they're observed only for smaller particles suggests size-dependent neutralisation is occurring. Tomlinson et al., also came to this conclusion based on volatility measurements of Aitken and accumulation mode marine particles (Tomlinson et al., 2007). They suggested it could be explained by sulphuric acid being added to the aerosol by in-cloud aqueous phase processes faster than it can be neutralized by limited available ammonia, leading to less-neutralised accumulation mode particles and more-neutralised Aitken mode particles. On the other hand, smaller particles may simply be neutralized by limited ammonia more readily due to their higher surface-volume ratio (Biskos et al., 2009; McMurry et al., 1983).

The large hygroscopic growth generally displayed by marine aerosol particles suggests they contain large soluble fractions and are efficient CCN. This is indeed the case and critical dry diameters of only ~65–90 nm are required for marine aerosol activation at 0.2% supersaturation (Andreae and Rosenfeld, 2008). This means large fractions of marine aerosols are capable of forming cloud droplets even at the low supersaturation values (0.1–0.3%) typically achieved in the MBL (Hegg et al., 2009; Hudson and Li, 1995). It is also why a well defined minimum is frequently observed at around 80 nm in marine aerosol number size distributions (the Hoppel minimum, see section 2.2.2).

Finally, special mention needs to be made of HTDMA studies investigating the hygroscopic growth of freshly formed particles during coastal nucleation events (Asmi et al., 2010; Johnson et al., 2005; Väkevä et al., 2002). Vakeva et al., measured $HGF_{90\%}$ between 1 and 1.1 for freshly nucleated particles (d_p 8–10 nm) at Mace Head, Ireland. This growth is well below that displayed by sulphate particles of the same size. For example, ammonium sulphate particles in this size range have $HGF_{90\%}$ of around 1.4 (considerably less than HGF for 100 nm ammonium sulphate particles in Fig.2.3 because the Kelvin effect acts to decrease *HGF* with decreasing particle diameter). This was one of the main lines of evidence suggesting that iodine- rather than sulphate-related particle formation occurs at Mace Head (O'Dowd and Hoffmann, 2005), because iodine-containing compounds are not as hygroscopic as sulphates (Ristovski et al., 2006). However, similar observations at a sub-tropical coastal site (Johnson et al., 2005) and near-coastal Antarctic site (Asmi et al., 2010) showed *HGFs* (and volatilisation behaviour in the Johnson et al. study) mainly consistent with ammoniated sulphate particles possibly mixed with an organic component.

2.5 Research needs to be addressed in this project

Based on this literature review a number of gaps in our understanding of marine aerosols and the way they interact with water vapour can be identified and will be discussed in this section. Prior to indentifying specific gaps in knowledge the first general point to make is that *there is a large gap in the knowledge of marine aerosols that can only be filled by more observations*. While our conceptual framework of marine aerosols is becoming relatively developed (particularly after recent studies into the role of primary and secondary organics) there is a need for it to be validated by many more field observations than have currently been made. The main reason for the lack of observations is the logistical issues involved in taking sophisticated aerosol measurements over the oceans. Specialised and highly equipped vessels are needed and these involve significant operational costs. In many cases these difficulties are sidestepped by anchoring marine aerosol studies to coastal laboratories along with an educated hope that air masses arrive at the measurement site from over the open oceans. This was the approach taken in this PhD program, which had the broad aim of collecting additional data on marine aerosols and their ability to absorb water vapour. Specifically, the following research needs were identified as being worthy of further investigation.

The influence of organics on water uptake by marine aerosols

Over the last decade many laboratory and modelling studies have advanced our understanding of the ways in which various organic compounds can influence both the thermodynamics and kinetics of aerosol water uptake. It is also known that marine aerosols can potentially contain significant fractions of organic material and some of the specific organic compounds or classes of compounds that comprise this matter have even been identified. However, these compositional data are limited and, on the scale of the World Ocean, extremely scarce. In general it is also poorly size-resolved (i.e. only sub- or super-micrometre concentrations) so we cannot judge whether or not organic material is concentrated at particle sizes where it would have the largest influence on climate-relevant aerosol properties (e.g. around critical CCN activation diameters). Therefore, it is still difficult to apply our understanding of water uptake by organic aerosols to the marine aerosol system. This means the water uptake properties of marine aerosols are still poorly understood over a wide range of different atmospheric and oceanic conditions.

One way to help fill this gap in the knowledge is to examine the formation and composition of marine aerosols. In particular, there is a need to collect highly size-resolved data on the relative concentrations and mixing states of organic and inorganic aerosols. This point is discussed in more detail below with reference to both primary and secondary marine/coastal aerosols. Another option to address the gap in knowledge is to directly measure the hygroscopic properties of marine aerosol particles. These measurements need to be taken in combination with others (e.g. chemical composition, volatility) so that the influence of organics on the hygroscopic growth can be discerned. Methodologies should be employed that examine the timescales of water uptake to judge whether or not kinetic effects are significant. A single instrument that is capable of doing all this is the VH-TDMA.

Coastal nucleation events

Coastal nucleation events have been observed frequently around the world but they have only been comprehensively characterised at a few locations. Therefore, much of what is known about the mechanisms behind coastal particle production has been derived from research at only a few locations, the most famous being Mace Head in Ireland. To remedy this situation and determine whether similar particle production occurs in other regions and climate zones around the world dedicated measurement campaigns are required along previously unstudied coastal stretches. At the very least these studies need to determine the frequency with which nucleation events occur, the meteorological and tidal conditions that are conducive to event occurrence, and the physical characteristics (e.g. size distribution) of freshly nucleated particles as a function of time.

In addition, more attention needs to be paid to the chemical species involved in coastal particle formation and growth to climatically-relevant sizes. The comprehensive work conducted at Mace Head has shown that iodine-containing compounds drive particle formation and growth at this site but sulphates and organics probably also contribute, particularly during the growth phase. To determine whether this is the case at other coastal locations compositional data are required for freshly nucleated particles. This is extremely difficult to obtain because nucleation mode particle mass concentrations are incredibly small even if number concentrations are very high. In this regard, number-based methods for investigating chemical composition (such as the VH-TDMA) are preferable. However, even these are limited by the ability to detect particles less than ~3 nm in condensation particle counters. This means they are unable to investigate the chemical species involved in the initial particle formation and growth stages. However, they are able to examine the composition of larger nucleation mode particles. This is still very important because it indicates how nucleation mode particles grow up to the Aitken mode and beyond where they participate in the direct and indirect effects of aerosols on climate.

Sea spray aerosols

It is well known that sea spray particles contain both an inorganic (sea salt) and organic fraction. However, there is still a lack of size-resolved data on the relative concentrations of organics and inorganics in sea spray aerosol. Such information is particularly wanting for accumulation mode particles. Size-resolved impactor measurements have suggested that accumulation mode sea spray particles are up to 80% organic (Facchini et al., 2008b; Keene et al., 2007a) but measurements of their water uptake properties are not consistent with an organic fraction of this magnitude (Fuentes et al., 2010; Sellegri et al., 2008). Further measurements are required to resolve this discrepancy. It is critical that this happens because accumulation mode particles are the most numerous fraction of sea spray aerosol and they play a large role in both the direct and indirect effects of marine aerosols on climate. Determining their organic fraction will determine their size and phase as a function of RH and also their ability to act as CCN.

Instrumentation

It is suggested that the VH-TDMA is one instrument that is suitable for addressing many of the research needs identified above. It can be employed in a wide range of different environments, it is able to investigate the effects that volatile organic components have on the hygroscopic growth of ultrafine particles (10 nm < d_p < 200 nm), and it is also able to infer the chemical composition of such particles, including their mixing state. However, this is a relatively new measurement technique and further studies are required to develop its potential. Marine aerosols are a good target for VH-TDMA studies because they are thought to consist of only a few classes of compounds, each of which has very different combined volatile and hygroscopic properties. This means a lot of compositional data can be gained from comparing the VH-TDMA scans of ambient marine particles with those of laboratory-generated particles of precisely known composition. However, this comparative approach ultimately needs to be validated against independent measurements of particle chemical composition. For example, a study is required that compares the conclusions drawn from VH-TMDA measurements to high-time-resolution aerosol mass spectrometry (AMS) measurements. AMS is an accepted and now widely used method for measuring the chemical composition of sub-micrometre non-refractory aerosols.

2.6 References

Abbatt, J. P. D., Broekhuizen, K., and Kumal, P. P.: Cloud condensation nucleus activity of internally mixed ammonium sulfate/organic acid aerosol particles, Atmospheric Environment, 39(26), 4767-4778, 10.1016/j.atmosenv.2005.04.029, 2005.

Aitken, J.: On Dust, Fogs and Clouds, Transactions of the Royal Society of Edinburgh, XXX (I), 337-368, 1880.

Aitken, J.: On some Nuclei of Cloudy Condensation (Part II), Transactions of the Royal Society of Edinburgh, XXXIX (III), 15-25, 1897.

Allan, J. D., Topping, D. O., Good, N., Irwin, M., Flynn, M., Williams, P. I., Coe, H., Baker, A. R., Martino, M., Niedermeier, N., Wiedensohler, A., Lehmann, S., Muller, K., Herrmann, H., and McFiggans, G.: Composition and properties of atmospheric particles in the eastern Atlantic and impacts on gas phase uptake rates, Atmospheric Chemistry and Physics, 9(23), 9299-9314, 2009.

Aller, J. Y., Kuznetsova, M. R., Jahns, C. J., and Kemp, P. F.: The sea surface microlayer as a source of viral and bacterial enrichment in marine aerosols, J. Aerosol. Sci., 36(5-6), 801-812, 10.1016/j.jaerosci.2004.10.012, 2005.

Andreae, M. O., and Rosenfeld, D.: Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, Earth Science Reviews, 89(1-2), 13-41, 10.1016/j.earscirev.2008.03.001, 2008.

Andreas, E. L.: A new sea spray generation function for wind speeds up to 32m s(-1), Journal of Physical Oceanography, 28(11), 2175-2184, 1998.

Andrews, E., and Larson, S. M.: Effect of surfactant layers on the size changes of aerosol particles as a function of relative humidity, Environ. Sci. Technol., 27(5), 857-865, 1993.

Arnold, S. R., Spracklen, D. V., Williams, J., Yassaa, N., Sciare, J., Bonsang, B., Gros, V., Peeken, I., Lewis, A. C., Alvain, S., and Moulin, C.: Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol, Atmospheric Chemistry and Physics, 9(4), 1253-1262, 2009.

Asmi, E., Frey, A., Virkkula, A., Ehn, M., Manninen, H. E., Timonen, H., Tolonen-Kivimaki, O., Aurela, M., Hillamo, R., and Kulmala, M.: Hygroscopicity and chemical composition of Antarctic sub-micrometre aerosol particles and observations of new particle formation, Atmospheric Chemistry and Physics, 10(9), 4253-4271, 10.5194/acp-10-4253-2010, 2010.

Ayers, G. P., Ivey, J. P., and Gillet, R. W.: Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air, Nature, 349(6308), 404-406, 1991.

Badger, C. L., George, I., Griffiths, P. T., Braban, C. F., Cox, R. A., and Abbatt, J. P. D.: Phase transitions and hygroscopic growth of aerosol particles containing humic acid and mixtures of humic acid and ammonium sulphate, Atmospheric Chemistry and Physics, 6, 755-768, 2006.

Baltensperger, U., Kalberer, M., Dommen, J., Paulsen, D., Alfarra, M. R., Coe, H., Fisseha, R., Gascho, A., Gysel, M., Nyeki, S., Sax, M., Steinbacher, M., Prevot, A. S. H., Sjogren, S., Weingartner, E., and Zenobi, R.: Secondary organic aerosols from anthropogenic and biogenic precursors, Faraday Discuss., 130, 265-278, 10.1039/b417367h, 2005.

Barker, D. R., and Zeitlin, H.: Metal-Ion Concentrations in Sea-Surface Microlayer and Size-Separated Atmospheric Aerosol Samples in Hawaii, J. Geophys. Res., 77(27), 5076-5086, 1972.

Barnes, G. T.: The effects of monolayers on the evaporation of liquids, Advances in Colloid and Interface Science, 25, 89-200, 1986.

Barnes, I., Hjorth, J., and Mihalopoulos, N.: Dimethyl sulfide and dimethyl sulfoxide and their oxidation in the atmosphere, Chem. Rev., 106(3), 940-975, 10.1021/cr020529+, 2006.

Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J., and Stoiber, R. E.: Sulfur emissions to the Atmosphere from Natural Sources, Journal of Atmospheric Chemistry, 14, 315-337, 1992.

Bates, T. S., Kapustin, V. N., Quinn, P. K., Covert, D. S., Coffman, D. J., Mari, C., Durkee, P. A., De Bruyn, W. J., and Saltzman, E. S.: Processes controlling the distribution of aerosol particles in the lower marine boundary layer during the First Aerosol Characterization Experiment (ACE 1), J. Geophys. Res., 103, 16,369–316,383, 1998.

Berg, O. H., Swietlicki, E., and Krejci, R.: Hygroscopic growth of aerosol particles in the marine boundary layer over the Pacific and Southern Oceans during the First Aerosol Characterization Experiment (ACE 1), J. Geophys. Res., 103(D13), 16535-16545, 10.1029/97jd02851, 1998.

Bigg, E. K., Brownscombe, J. L., and Thompson, W. J.: Fog modification with long-chain alcohols, Journal of Applied Meteorology, 8, 75-82, 1969.

Bigg, E. K., and Turvey, D. E.: Sources of atmospheric particles over Australia, Atmospheric Environment, 12(8), 1643-1655, 1978.

Bigg, E. K., and Leck, C.: Properties of the aerosol over the central Arctic Ocean, Journal of Geophysical Research, 106(D23), 32101-32109, 2001.

Bigg, E. K., Leck, C., and Tranvik, L.: Particulates of the surface microlayer of open water in the central Arctic Ocean in summer, Mar. Chem., 91(1-4), 131-141, 10.1016/j.marchem.2004.06.005, 2004.

Bigg, E. K.: Sources, nature and influence on climate of marine airborne particles, Environmental Chemistry, 4(3), 155-161, 10.1071/en07001, 2007.

Bigg, E. K., and Leck, C.: The composition of fragments of bubbles bursting at the ocean surface, J. Geophys. Res., 113(D11), D11209, 10.1029/2007jd009078, 2008.

Bilde, M., and Svenningsson, B.: CCN activation of slightly soluble organics: the importance of small amounts of inorganic salt and particle phase, Tellus Ser. B-Chem. Phys. Meteorol., 56(2), 128-134, 2004.

Biskos, G., Malinowski, A., Russell, L. M., Buseck, P. R., and Martin, S. T.: Nanosize effect on the deliquescence and the efflorescence of sodium chloride particles, Aerosol Sci. Technol., 40(2), 97-106, 10.1080/02786820500484396, 2006a.

Biskos, G., Paulsen, D., Russell, L. M., Buseck, P. R., and Martin, S. T.: Prompt deliquescence and efflorescence of aerosol nanoparticles, Atmospheric Chemistry and Physics, 6, 4633-4642, 2006b.

Biskos, G., Russell, L. M., Buseck, P. R., and Martin, S. T.: Nanosize effect on the hygroscopic growth factor of aerosol particles, Geophys. Res. Lett., 33(7), L07801, 10.1029/2005gl025199, 2006c.

Biskos, G., Buseck, P. R., and Martin, S. T.: Hygroscopic growth of nucleation-mode acidic sulfate particles, J. Aerosol. Sci., 40(4), 338-347, 10.1016/j.jaerosci.2008.12.003, 2009.

Blanchard, D. C.: Sea-to-Air Transport of Surface Active Material, Science, 146, 396-397, 10.1126/science.146.3642.396, 1964.

Blanchard, D. C.: The ejection of drops from the sea their enrichment with bacteria and other materials: A review, Estuaries, 12(3), 127-137, 1989.

Bonsang, B., Polle, C., and Lambert, G.: Evidence for marine production of isoprene, Geophys. Res. Lett., 19(11), 1129-1132, 10.1029/92gl00083, 1992.

Boyce, S. G.: Source of Atmospheric Salts, Science, 113, 620-621, 1951.

Braban, C. F., Carroll, M. F., Styler, S. A., and Abbatt, J. P. D.: Phase transitions of malonic and oxalic acid aerosols, J. Phys. Chem. A, 107(34), 6594-6602, 10.1021/jp034483f, 2003.

Brechtel, F. J., and Kreidenweis, S. M.: Predicting particle critical supersaturation from hygroscopic growth measurements in the humidified TDMA. part I: Theory and sensitivity studies, J. Atmos. Sci., 57(12), 1854-1871, 2000.

Broekhuizen, K., Kumar, P. P., and Abbatt, J. P. D.: Partially soluble organics as cloud condensation nuclei: Role of trace soluble and surface active species, Geophys. Res. Lett., 31(1), L01107, 10.1029/2003gl018203, 2004.

Brooks, S. D., Wise, M. E., Cushing, M., and Tolbert, M. A.: Deliquescence behavior of organic/ammonium sulfate aerosol, Geophysical Research Letters, 29(19), 4, 191710.1029/2002gl014733, 2002.

Brooks, S. D., DeMott, P. J., and Kreidenweis, S. M.: Water uptake by particles containing humic materials and mixtures of humic materials with ammonium sulfate, Atmospheric Environment, 38(13), 1859-1868, 10.1016/j.atmosenv.2004.01.009, 2004.

Cainey, J., and Harvey, M.: Dimethylsulfide, a limited contributor to new particle formation in the clean marine boundary layer, Geophysical Research Letters, 29(7), 4, 1128 10.1029/2001gl014439, 2002.

Capaldo, K., Corbett, J. J., Kasibhatla, P., Fischbeck, P., and Pandis, S. N.: Effects of ship emissions on sulphur cycling and radiative climate forcing over the ocean, Nature, 400(6746), 743-746, 1999.

Cavalli, F., Facchini, M. C., Decesari, S., Mircea, M., Emblico, L., Fuzzi, S., Ceburnis, D., Yoon, Y. J., O'Dowd, C. D., Putaud, J. P., and Dell'Acqua, A.: Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic, Journal of Geophysical Research, 109, 16, D24215 10.1029/2004jd005137, 2004.

Ceburnis, D., O'Dowd, C. D., Jennings, G. S., Facchini, M. C., Emblico, L., Decesari, S., Fuzzi, S., and Sakalys, J.: Marine aerosol chemistry gradients: Elucidating primary and secondary processes and fluxes, Geophys. Res. Lett., 35(7), L07804, 10.1029/2008gl033462, 2008.

Chan, C. K., Kwok, C. S., and Chow, A. H. L.: Study of hygroscopic properties of aqueous mixtures of disodium fluorescein and sodium chloride using an electrodynamic balance, Pharm. Res., 14(9), 1171-1175, 1997.

Chan, M. N., and Chan, C. K.: Hygroscopic properties of two model humic-like substances and their mixtures with inorganics of atmospheric importance, Environ. Sci. Technol., 37(22), 5109-5115, 10.1021/es034272o, 2003.

Chan, M. N., and Chan, C. K.: Mass transfer effects in hygroscopic measurements of aerosol particles, Atmospheric Chemistry and Physics, 5, 2703-2712, 2005.

Chan, M. N., and Chan, C. K.: Mass transfer effects on the hygroscopic growth of ammonium sulfate particles with a water-insoluble coating, Atmospheric Environment, 41(21), 4423-4433, 10.1016/j.atmosenv.2007.01.047, 2007.

Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, Nature, 326, 655-661, 1987.

Chen, H., Sangster, J., Teng, T. T., and Lenzi, F.: A general method of predicting the water activity of ternary aqueous solutions from binary data, Can. J. Chem. Eng., 51(2), 234-241, 1973.

Chin, M., and Jacob, D. J.: Anthropogenic and natural contributions to tropospheric sulfate: A global model analysis, J. Geophys. Res.-Atmos., 101(D13), 18691-18699, 1996.

Choi, M. Y., and Chan, C. K.: The effects of organic species on the hygroscopic behaviors of inorganic aerosols, Environ. Sci. Technol., 36(11), 2422-2428, 10.1021/es0113293, 2002.

Chuang, P. Y., Charlson, R. J., and Seinfeld, J. H.: Kinetic limitations on droplet formation in clouds, Nature, 390(6660), 594-596, 1997.

Chuang, P. Y.: Measurement of the timescale of hygroscopic growth for atmospheric aerosols, Journal of Geophysical Research, 108(D9), 4282, 10.1029/2002jd002757, 2003.

Claeys, M., Wang, W., Vermeylen, R., Kourtchev, I., Chi, X. G., Farhat, Y., Surratt, J. D., Gomez-Gonzalez, Y., Sciare, J., and Maenhaut, W.: Chemical characterisation of marine aerosol at Amsterdam Island during the austral summer of 2006-2007, J. Aerosol. Sci., 41(1), 13-22, 10.1016/j.jaerosci.2009.08.003, 2010.

Clarke, A. D., Davis, D., Kapustin, V. N., Eisele, F., Chen, G., Paluch, I., Lenschow, D., Bandy, A. R., Thornton, D., Moore, K., Mauldin, L., Tanner, D., Litchy, M., Carroll, M. A., Collins, J., and Albercook, C.: Particle nucleation in the tropical boundary layer and its coupling to marine sulfur sources, Science, 282(5386), 89-92, 1998a.

Clarke, A. D., Varner, J. L., Eisele, F., Mauldin, R. L., Tanner, D., and Litchy, M.: Particle production in the remote marine atmosphere: Cloud outflow and subsidence during ACE 1, J. Geophys. Res., 103(D13), 16397-16409, 10.1029/97jd02987, 1998b.

Clarke, A. D., Kapustin, V. N., Eisele, F. L., Weber, R. J., and McMurry, P. H.: Particle production near marine clouds: Sulfuric acid and predictions from classical binary nucleation, Geophys. Res. Lett., 26(16), 2425-2428, 10.1029/1999gl900438, 1999.

Clarke, A. D., and Kapustin, V. N.: A Pacific Aerosol Survey. Part I: A Decade of Data on Particle Production, Transport, Evolution, and Mixing in the Troposphere, J. Atmos. Sci., 59, 363-382, 2002.

Clarke, A. D., Owens, S. R., and Zhou, J.: An ultrafine sea-salt flux from breaking waves: Implications for cloud condensation nuclei in the remote marine atmosphere, Journal of Geophysical Research, 111, D06202, doi:10.1029/2005JD006565, 2006.

Clegg, S. L., Pitzer, K. S., and Brimblecombe, P.: Thermodynamics of multicomponent, miscible, ionic solutions 2. Mixtures including unsymmetrical electrolytes, J. Phys. Chem., 96(23), 9470-9479, 1992.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H+-NH4+-Na+-SO42--NB3--Cl--H2O at 298.15 K, J. Phys. Chem. A, 102(12), 2155-2171, 1998a.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H+-NH4+-SO42--NO3--H2O at tropospheric temperatures, J. Phys. Chem. A, 102(12), 2137-2154, 1998b.

Clegg, S. L., Seinfeld, J. H., and Brimblecombe, P.: Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds, J. Aerosol. Sci., 32(6), 713-738, 2001.

Coe, H., Williams, P. I., McFiggans, G., Gallagher, M. W., Beswick, K. M., Bower, K. N., and Choularton, T. W.: Behavior of ultrafine particles in continental and marine air masses at a rural site in the United Kingdom, J. Geophys. Res., 105(D22), 26891-26905, 10.1029/2000jd900234, 2000.

Covert, D. S., Kapustin, V. N., Bates, T. S., and Quinn, P. K.: Physical properties of marine boundary layer aerosol particles of the mid-Pacific in relation to sources and meteorological transport, J. Geophys. Res., 101, 6919–6930, 1996.

Cruz, C. N., and Pandis, S. N.: Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol, Environ. Sci. Technol., 34(20), 4313-4319, 10.1021/es9907109, 2000.

Cubison, M. J., Coe, H., and Gysel, M.: A modified hygroscopic tandem DMA and a data retrieval method based on optimal estimation, J. Aerosol. Sci., 36(7), 846-865, 10.1016/j.jaerosci.2004.11.009, 2005.

Cziczo, D. J., Nowak, J. B., Hu, J. H., and Abbatt, J. P. D.: Infrared spectroscopy of model tropospheric aerosols as a function of relative humidity: Observation of deliquescence and crystallization, J. Geophys. Res., 102(D15), 18843-18850, 10.1029/97jd01361, 1997.

Davis, E. J., Buehler, M. F., and Ward, T. L.: The double-ring electrodynamic balance for microparticle characterization, Review of Scientific Instruments, 61(4), 1281, 1990.

de Reus, M., Krejci, R., Williams, J., Fischer, H., Scheele, R., and Ström, J.: Vertical and horizontal distributions of the aerosol number concentration and size distribution over the northern Indian Ocean, J. Geophys. Res., 106, 28,629–628,641, 2001.

Deane, G. B., and Stokes, M. D.: Scale dependence of bubble creation mechanisms in breaking waves, Nature, 418(6900), 839-844, 10.1038/nature00967, 2002.

Dick, W. D., Saxena, P., and McMurry, P. H.: Estimation of water uptake by organic compounds in submicron aerosols measured during the Southeastern Aerosol and Visibility Study, J. Geophys. Res., 105(D1), 1471-1479, 10.1029/1999jd901001, 2000.

Dinar, E., Taraniuk, I., Graber, E. R., Katsman, S., Moise, T., Anttila, T., Mentel, T. F., and Rudich, Y.: Cloud Condensation Nuclei properties of model and atmospheric HULIS, Atmospheric Chemistry and Physics, 6, 2465-2481, 2006.

Donaldson, D. J., and Vaida, V.: The influence of organic films at the air-aqueous boundary on atmospheric processes, Chem. Rev., 106(4), 1445-1461, 10.1021/cr040367c, 2006.

Duplissy, J., Gysel, M., Sjogren, S., Meyer, N., Good, N., Kammermann, L., Michaud, V., Weigel, R., Martins dos Santos, S., Gruening, C., Villani, P., Laj, P., Sellegri, K., Metzger, A., McFiggans, G. B., Wehrle, G., Richter, R., Dommen, J., Ristovski, Z., Baltensperger, U., and Weingartner, E.: Intercomparison study of six HTDMAs: results and recommendations, Atmospheric Measurement Techniques, 2(2), 363 - 378, 2009.

Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F., Hings, S., Jung, D., Borrmann, S., and Andreae, M. O.: Size matters more than chemistry for cloud-nucleating ability of aerosol particles, Science, 312(5778), 1375-1378, 10.1126/science.1125261, 2006.

Ebert, M., Inerle-Hof, M., and Weinbruch, S.: Environmental scanning electron microscopy as a new technique to determine the hygroscopic behaviour of individual aerosol particles, Atmospheric Environment, 36(39-40), 5909-5916, 2002.

Erdakos, G. B., Chang, E. I., Pankow, J. F., and Seinfeld, J. H.: Prediction of activity coefficients in liquid aerosol particles containing organic compounds, dissolved inorganic salts, and water - Part 3: Organic compounds, water, and ionic constituents by consideration of short-, mid-, and long-range effects using X-UNIFAC.3, Atmospheric Environment, 40(33), 6437-6452, 10.1016/j.atmosenv.2006.04.001, 2006.

Ervens, B., Feingold, G., and Kreidenweis, S. M.: Influence of water-soluble organic carbon on cloud drop number concentration, J. Geophys. Res., 110(D18), D18211, 10.1029/2004jd005634, 2005.

Facchini, M. C., Mircea, M., Fuzzi, S., and Charlson, R. J.: Cloud albedo enhancement by surface-active organic solutes in growing droplets, Nature, 401(6750), 257-259, 1999.

Facchini, M. C., Decesari, S., Mircea, M., Fuzzi, S., and Loglio, G.: Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition, Atmospheric Environment, 34(28), 4853-4857, 2000.

Facchini, M. C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D., and O'Dowd, C. D.: Important Source of Marine Secondary Organic Aerosol from Biogenic Amines, Environ. Sci. Technol., 42(24), 9116-9121, 10.1021/es8018385, 2008a.

Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophysical Research Letters, 35, L17814, doi:10.1029/2008GL034210, 2008b.

Feingold, G., and Chuang, P. Y.: Analysis of the influence of film-forming compounds on droplet growth: Implications for cloud microphysical processes and climate, J. Atmos. Sci., 59(12), 2006-2018, 2002.

Fierz-Schmidhauser, R., Zieger, P., Wehrle, G., Jefferson, A., Ogren, J. A., Baltensperger, U., and Weingartner, E.: Measurement of relative humidity dependent light scattering of aerosols, Atmospheric Measurement Techniques, 3(1), 39-50, 2010.

Finlayson-Pitts, B. J., and Hemminger, J. C.: Physical chemistry of airborne sea salt particles and their components, J. Phys. Chem. A, 104(49), 11463-11477, 10.1021/jp002968n, 2000.

Fitzgerald, J. W.: Marine aerosols: A review, Atmospheric Environment, 25, 533-545, 1991.

Fletcher, C. A., Johnson, G. R., Ristovski, Z. D., and Harvey, M.: Hygroscopic and volatile properties of marine aerosol observed at Cape Grim during the P2P campaign, Environmental Chemistry, 4, 162-171, 2007.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R.: Changes in Atmospheric Constituents and in Radiative Forcing, in: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change edited by: Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller, Cambridge University Press, Cambridge, United Kingdom, 2007.

Fredenslund, A., Jones, R. L., and Prausnitz, J. M.: Group contribution estimation of activity coefficients in non-ideal liquid mixtures, Aiche J., 21, 1086-1098, 1975.

Fuentes, E., Coe, H., Green, D., De Leeuw, G., and McFiggans, G.: Laboratory-generated primary marine aerosol via bubble-bursting and atomization, Atmospheric Measurement Techniques, 3, 141-162, 2010.

Gantt, B., Meskhidze, N., and Kamykowski, D.: A new physically-based quantification of marine isoprene and primary organic aerosol emissions, Atmospheric Chemistry and Physics, 9(14), 4915-4927, 2009.

Gantt, B., Meskhidze, N., and Carlton, A. G.: The impact of marine organics on the air quality of the western United States, Atmospheric Chemistry and Physics Discussions, 10(3), 6257-6278, 2010.

Gao, J., Wang, T., Zhou, X. H., Wu, W. S., and Wang, W. X.: Measurement of aerosol number size distributions in the Yangtze River delta in China: Formation and growth of particles under polluted conditions, Atmospheric Environment, 43(4), 829-836, 10.1016/j.atmosenv.2008.10.046, 2009.

Gershey, R. M.: Characterization of seawater organic matter carried by bubble-generated aerosols, Limnol. Oceanogr., 28(2), 309-319, 1983.

Gibb, S. W., Mantoura, R. F. C., and Liss, P. S.: Ocean-atmosphere exchange and atmospheric speciation of ammonia and methylamines in the region of the NW Arabian Sea, Global Biogeochem. Cycles, 13(1), 161-178, 10.1029/98gb00743, 1999.

Gill, P. S., Graedel, T. E., and Weschler, C. J.: Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops and snowflakes, Reviews of Geophysics and Space Physics, 21(4), 903-920, 1983.

Gong, S. L.: A parameterization of sea-salt aerosol source function for sub- and super-micron particles, Global Biogeochem. Cycles, 17(4), 1097, 10.1029/2003gb002079, 2003.

Good, N., Topping, D. O., Duplissy, J., Gysel, M., Meyer, N. K., Metzger, A., Turner, S. F., Baltensperger, U., Ristovski, Z., Weingartner, E., Coe, H., and McFiggans, G.: Widening the gap between measurement and modelling of secondary organic aerosol properties?, Atmospheric Chemistry and Physics, 10(6), 2577-2593, 2010.

Gorbunov, B., and Hamilton, R.: Water nucleation on aerosol particles containing both soluble and insoluble substances, J. Aerosol. Sci., 28(2), 239-248, 1997.

Gorbunov, B., Hamilton, R., Clegg, N., and Toumi, R.: Water nucleation on aerosol particles containing both organic and soluble inorganic substances, Atmospheric Research, 47-48, 271-283, 1998.

Gras, J. L., Jimi, S. I., Siems, S. T., and Krummel, P. B.: Postfrontal nanoparticles at Cape Grim: observations, Environmental Chemistry, 6(6), 508-514, 10.1071/en09075, 2009.

Gysel, M., Weingartner, E., Nyeki, S., Paulsen, D., Baltensperger, U., Galambos, I., and Kiss, G.: Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol, Atmospheric Chemistry and Physics, 4, 35-50, 2004.

Gysel, M., McFiggans, G. B., and Coe, H.: Inversion of tandem differential mobility analyser (TDMA) measurements, J. Aerosol. Sci., 40(2), 134-151, 10.1016/j.jaerosci.2008.07.013, 2009.

Hameri, K., Vakeva, M., Aalto, P. P., Kulmala, M., Swietlicki, E., Zhou, J., Seidl, W., Becker, E., and O'Dowd, C. D.: Hygroscopic and CCN properties of aerosol particles in boreal forests, Tellus Series B, 53(4), 359-379, 2001.

Hameri, K., Charlson, R., and Hansson, H. C.: Hygroscopic properties of mixed ammonium sulfate and carboxylic acids particles, Aiche J., 48(6), 1309-1316, 2002.

Hämeri, K., Väkevä, M., Hansson, H.-C., and Laaksonen, A.: Hygroscopic growth of ultrafine ammonium sulphate aerosol measured using an ultrafine tandem differential mobility analyzer, J. Geophys. Res., 105(D17), 22231-22242, 10.1029/2000jd900220, 2000.

Hatch, C. D., Gierlus, K. M., Zahardis, J., Schuttlefield, J., and Grassian, V. H.: Water uptake of humic and fulvic acid: measurements and modelling using single parameter Kohler theory, Environmental Chemistry, 6(5), 380-388, 10.1071/en09083, 2009.

Hegg, D. A., Covert, D. S., Jonsson, H., and Covert, P. A.: An instrument for measuring size-resolved aerosol hygroscopicity at both sub- and super-micron sizes, Aerosol Sci. Technol., 41(9), 873-883, 10.1080/02786820701506955, 2007.

Hegg, D. A., Covert, D. S., Jonsson, H. H., and Woods, R.: Differentiating natural and anthropogenic cloud condensation nuclei in the California coastal zone, Tellus Series B, 61(4), 669-676, 10.1111/j.1600-0889.2009.00435.x, 2009.

Heintzenberg, J., Covert, D. C., and Van Dingenen, R.: Size distribution and chemical composition of marine aerosols: a compilation and review, Tellus Series B, 52(4), 1104-1122, 2000.

Heintzenberg, J., Birmili, W., Wiedensohler, A., Nowak, A., and Tuch, T.: Structure, variability and persistence of the submicrometre marine aerosol, Tellus Series B, 56(4), 357-367, 2004.

Hennig, T., Massling, A., Brechtel, F. J., and Wiedensohler, A.: A tandem DMA for highly temperature-stabilized hygroscopic particle growth measurements between 90% and 98% relative humidity, J. Aerosol. Sci., 36(10), 1210-1223, 10.1016/j.jaerosci.2005.01.005, 2005.

Henning, S., Rosenorn, T., D'Anna, B., Gola, A. A., Svenningsson, B., and Bilde, M.: Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt, Atmospheric Chemistry and Physics, 5, 575-582, 2005.

Hoffman, E. J., and Duce, R. A.: The Organic Carbon Content of Marine Aerosols Collected on Bermuda, J. Geophys. Res., 79(30), 4474-4477, 1974.

Hoffman, E. J., and Duce, R. A.: Factors Influencing the Organic Carbon Content of Marine Aerosols: A Laboratory Study, J. Geophys. Res., 81(21), 3667-3670, 1976.

Hoffmann, T., O'Dowd, C. D., and Seinfeld, J. H.: Iodine oxide homogeneous nucleation: An explanation for coastal new particle production, Geophys. Res. Lett., 28(10), 1949-1952, 10.1029/2000gl012399, 2001.

Hoppel, W. A., Frick, G. M., and Larson, R. E.: Effect of nonprecipitating clouds on the aerosol size distribution in the marine boundary layer, Geophysical Research Letters, 13(1), 125-128, 1986.

Hoppel, W. A., Fitzgerald, J. W., Frick, G. M., Larson, R. E., and Mack, E. J.: Aerosol size distributions and optical properties found in the marine moundary layer over the Atlantic Ocean, Journal of Geophysical Research, 95(D4), 3659-3686, 1990.

Hori, M., Ohta, S., Murao, N., and Yamagata, S.: Activation capability of water soluble organic substances as CCN, J. Aerosol. Sci., 34(4), 419-448, 10.1016/s0021-8502(02)00190-8, 2003.

Hudson, J. G., and Li, H. G.: Microphysical contrasts in Atlantic stratus, J. Atmos. Sci., 52(16), 3031-3040, 1995.

Hultin, K. A. H., Nilsson, E. D., Krejci, R., Mårtensson, E. M., Ehn, M., Hagström, Å., and de Leeuw, G.: In situ laboratory sea spray production during the Marine Aerosol Production 2006 cruise on the northeastern Atlantic Ocean, Journal of Geophysical Research, 115(D6), D06201, 10.1029/2009jd012522, 2010.

Hunter, K. A.: Chemistry of the sea-surface microlayer, in: The sea surface and global change, edited by: Liss, P. S., and Duce, R. D., Cambridge University Press, Cambridge, UK, 287-321, 1997.

Hyvarinen, A. P., Komppula, M., Engler, C., Kivekas, N., Kerminen, V. M., Dal Maso, M., Viisanen, Y., and Lihavainen, H.: Atmospheric new particle formation at Uto, Baltic Sea 2003-2005, Tellus Series B, 60(3), 345-352, 10.1111/j.1600-0889.2008.00343.x, 2008.

Jimenez, J. L., Bahreini, R., Cocker, D. R., III, Zhuang, H., Varutbangkul, V., Flagan, R. C., Seinfeld, J. H., O'Dowd, C. D., and Hoffmann, T.: New particle formation from photooxidation of diiodomethane (CH2I2), J. Geophys. Res., 108(D10), 4318, 10.1029/2002jd002452, 2003.

Jimi, S. I., Siems, S. T., McGregor, J. L., Gras, J. L., and Katzfey, J. J.: An investigation into the origin of aerosol nucleation events observed in the Southern Ocean boundary layer, Aust. Meteorol. Mag., 57(2), 85-93, 2008.

Johnson, G. R., Ristovski, Z., and Morawska, L.: Method for measuring the hygroscopic behaviour of lower volatiliy fractions in an internally mixed aerosol, J. Aerosol. Sci., 35, 443-455, 2004.

Johnson, G. R., Ristovski, Z. D., D'Anna, B., and Morawska, L.: Hygroscopic behaviour of partially volatilised coastal marine aerosols using the volatilisation and humidification tandem differential mobility analyser technique, Journal of Geophysical Research, 110, D20203, doi:10.1029/2004JD005657, 2005.

Johnson, G. R., Fletcher, C., Meyer, N., Modini, R., and Ristovski, Z. D.: A robust, portable H-TDMA for field use, J. Aerosol. Sci., 39(10), 850-861, 2008.

Jones, G. B., and Trevena, A. J.: The influence of coral reefs on atmospheric dimethylsulphide over the Great Barrier Reef, Coral Sea, Gulf of Papua and Solomon and Bismarck Seas, Mar. Freshw. Res., 56(1), 85-93, 10.1071/mf04097, 2005.

Joutsensaari, J., Vaattovaara, P., Vesterinen, M., Hameri, K., and Laaksonen, A.: A novel tandem differential mobility analyzer with organic vapor treatment of aerosol particles, Atmospheric Chemistry and Physics, 1, 51-60, 2001.

Juranyi, Z., Gysel, M., Duplissy, J., Weingartner, E., Tritscher, T., Dommen, J., Henning, S., Ziese, M., Kiselev, A., Stratmann, F., George, I., and Baltensperger, U.: Influence of gas-to-particle partitioning on the hygroscopic and droplet activation behaviour of alpha-pinene secondary organic aerosol, Phys. Chem. Chem. Phys., 11(36), 8091-8097, 10.1039/b904162a, 2009.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmospheric Chemistry and Physics, 5, 1053-1123, 2005.

Katoshevski, D., Nenes, A., and Seinfeld, J. H.: A study of processes that govern the maintenance of aerosols in the marine boundary layer, J. Aerosol. Sci., 30(4), 503-532, 1999.

Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl, E. E., Izaguirre, M. A., Davis, A. J., Long, M. S., Zhou, X., Smoydzin, L., and Sander, R.: Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface, Journal of Geophysical Research, 112, D21, doi:10.1029/2007JD008464, 2007a.

Keene, W. C., Stutz, J., Pszenny, A. A. P., Maben, J. R., Fischer, E. V., Smith, A. M., von Glasow, R., Pechtl, S., Sive, B. C., and Varner, R. K.: Inorganic chlorine and bromine in coastal New England air during summer, Journal of Geophysical Research, 112 (D10), D10S12, 10.1029/2006jd007689, 2007b.

Kiss, G., Tombacz, E., and Hansson, H. C.: Surface tension effects of humic-like substances in the aqueous extract of tropospheric fine aerosol, Journal of Atmospheric Chemistry, 50(3), 279-294, 10.1007/s10874-005-5079-5, 2005.

Koehler, K. A., Kreidenweis, S. M., DeMott, P. J., Prenni, A. J., Carrico, C. M., Ervens, B., and Feingold, G.: Water activity and activation diameters from hygroscopicity data - Part II: Application to organic species, Atmospheric Chemistry and Physics, 6, 795-809, 2006.

Kokkola, H., Sorjamaa, R., Peräniemi, A., Raatikainen, T., and Laaksonen, A.: Cloud formation of particles containing humic-like substances, Geophys. Res. Lett., 33(10), L10816, 10.1029/2006gl026107, 2006.

Kreidenweis, S. M., Koehler, K., DeMott, P. J., Prenni, A. J., Carrico, C., and Ervens, B.: Water activity and activation diameters from hygroscopicity data - Part I: Theory and application to inorganic salts, Atmospheric Chemistry and Physics, 5, 1357-1370, 2005.

Kudryavtsev, V. N., and Makin, V. K.: Model of the spume sea spray generation, Geophysical Research Letters, 36(6), L06801, 10.1029/2008gl036871, 2009.

Kulmala, M., Laaksonen, A., Korhonen, P., Vesala, T., Ahonen, T., and Barrett, J. C.: The Effect of Atmospheric Nitric Acid Vapor on Cloud Condensation Nucleus Activation, J. Geophys. Res., 98(D12), 22949-22958, 10.1029/93jd02070, 1993.

Kulmala, M., Laaksonen, A., and Pirjola, L.: Parameterizations for sulfuric acid/water nucleation rates, J. Geophys. Res., 103(D7), 8301-8307, 10.1029/97jd03718, 1998.

Kulmala, M., Korhonen, P., Napari, I., Karlsson, A., Berresheim, H., and O'Dowd, C. D.: Aerosol formation during PARFORCE: Ternary nucleation of H2SO4, NH3, and H2O, J. Geophys. Res., 107(D19), 8111, 10.1029/2001jd000900, 2002.

Kuznetsova, M., Lee, C., and Aller, J.: Characterization of the proteinaceous matter in marine aerosols, Mar. Chem., 96(3-4), 359-377, 10.1016/j.marchem.2005.03.007, 2005.

Laaksonen, A., Korhonen, P., Kulmala, M., and Charlson, R. J.: Modification of the K¨ohler equation to include soluble trace gases and slightly soluble substances, J. Atmos. Sci., 55, 853–862, 1998.

Laaksonen, A., Vesala, T., Kulmala, M., Winkler, P. M., and Wagner, P. E.: Commentary on cloud modelling and the mass accommodation coefficient of water, Atmospheric Chemistry and Physics, 5, 461-464, 2005.

Leck, C., Norman, M., Bigg, E. K., and Hillamo, R.: Chemical composition and sources of the high Arctic aerosol relevant for cloud formation, Journal of Geophysical Research, 107(D12), 18, 4135 10.1029/2001jc001463, 2002.

Leck, C., and Bigg, E. K.: Biogenic particles in the surface microlayer and overlaying atmosphere in the central Arctic Ocean during summer, Tellus Series B, 57(4), 305-316, 2005a.

Leck, C., and Bigg, E. K.: Source and evolution of the marine aerosol - A new perspective, Geophysical Research Letters, 32(19), 4, L19803 10.1029/2005gl023651, 2005b.

Leck, C., and Bigg, E. K.: Comparison of sources and nature of the tropical aerosol with the summer high Arctic aerosol, Tellus Series B, 60(1), 118-126, 10.1111/j.1600-0889.2007.00315.x, 2008.

Lee, Y. G., Lee, H. W., Kim, M. S., Choi, C. Y., and Kim, J.: Characteristics of particle formation events in the coastal region of Korea in 2005, Atmospheric Environment, 42(16), 3729-3739, 10.1016/j.atmosenv.2007.12.064, 2008.

Leifer, I., Caulliez, G., and de Leeuw, G.: Bubbles generated from wind-steepened breaking waves: 2. Bubble plumes, bubbles, and wave characteristics, J. Geophys. Res., 111(C6), C06021, 10.1029/2004jc002676, 2006.

Leifer, I., and de Leeuw, G.: Bubbles generated from wind-steepened breaking waves: 1. Bubble plume bubbles, J. Geophys. Res., 111(C6), C06020, 10.1029/2004jc002673, 2006.

Lewis, E. R., and Schwartz, S. E.: Sea salt aerosol production: Mechanisms, methods, measurements and models- A critical review, Geographical Monograph Series, American Geophysical Union, Washington, DC, 2004.

Liss, P. S., and Duce, R. D.: The sea surface and global change, Cambridge University Press, Cambridge, UK, 1997.

Liu, B. Y. H., Pui, D. Y. H., Whitby, K. T., Kittelson, D. B., Kousaka, Y., and McKenzie, R. L.: The aerosol mobility chromatograph: A new detector for sulfuric acid aerosols, Atmospheric Environment, 12(1-3), 99-104, 1978.

Mäkelä, J. M., Hoffmann, T., Holzke, C., Väkevä, M., Suni, T., Mattila, T., Aalto, P. P., Tapper, U., Kauppinen, E. I., and O'Dowd, C. D.: Biogenic iodine emissions and identification of end-products in coastal ultrafine particles during nucleation bursts, J. Geophys. Res., 107(D19), 8110, 10.1029/2001jd000580, 2002.

Marcolli, C., Luo, B. P., and Peter, T.: Mixing of the organic aerosol fractions: Liquids as the thermodynamically stable phases, J. Phys. Chem. A, 108(12), 2216-2224, 10.1021/jp0360801, 2004.

Martensson, E. M., Nilsson, E. D., de Leeuw, G., Cohen, L. H., and Hansson, H. C.: Laboratory simulations and parameterization of the primary marine aerosol production, J. Geophys. Res., 108, 4297, doi:10.1029/2002JD002263, 2003.

Matsumoto, K., Tanaka, H., Nagao, I., and Ishizaka, Y.: Contribution of particulate sulfate and organic carbon to cloud condensation nuclei in the marine atmosphere, Geophys. Res. Lett., 24(6), 655-658, 10.1029/97gl00541, 1997.

McFiggans, G., Plane, J. M. C., Allan, B. J., Carpenter, L. J., Coe, H., and O'Dowd, C.: A modeling study of iodine chemistry in the marine boundary layer, Journal of Geophysical Research, 105(D11), 14371-14385, 2000.

McFiggans, G., Coe, H., Burgess, R., Allan, J., Cubison, M., Alfarra, M. R., Saunders, R., Saiz-Lopez, A., Plane, J. M. C., Wevill, D. J., Carpenter, L. J., Rickard, A. R., and Monks, P. S.: Direct evidence for coastal iodine particles from Laminaria macroalgae - linkage to emissions of molecular iodine, Atmospheric Chemistry and Physics, 4, 701-713, 2004.

McFiggans, G.: Marine aerosols and iodine emissions, Nature, 433(7026), E13-E13, 10.1038/nature03372, 2005.

McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M. C., Feingold, G., Fuzzi, S., Gysel, M., Laaksonen, A., Lohmann, U., Mentel, T. F., Murphy, D. M., O'Dowd, C. D., Snider, J. R., and Weingartner, E.: The effect of physical and chemical aerosol properties on warm cloud droplet activation, Atmospheric Chemistry and Physics, 6, 2593-2649, 2006.

McFiggans, G., Bale, C. S. E., Ball, S. M., Beames, J. M., Bloss, W. J., Carpenter, L. J., Dorsey, J., Dunk, R., Flynn, M. J., Furneaux, K. L., Gallagher, M. W., Heard, D. E., Hollingsworth, A. M., Hornsby, K., Ingham, T., Jones, C. E., Jones, R. L., Kramer, L. J., Langridge, J. M., Leblanc, C., LeCrane, J. P., Lee, J. D., Leigh, R. J., Longley, I., Mahajan, A. S., Monks, P. S., Oetjen, H., Orr-Ewing, A. J., Plane, J. M. C., Potin, P., Shillings, A. J. L., Thomas, F., von Glasow, R., Wada, R., Whalley, L. K., and Whitehead, J. D.: Iodine-mediated coastal particle formation: an overview of the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) Roscoff coastal study, Atmospheric Chemistry and Physics, 10(6), 2975-2999, 2010.

McGovern, F. M., Jennings, S. G., and Oconnor, T. C.: Aerosol and trace gas measurements during the Mace Head experiment, Atmospheric Environment, 30(22), 3891-3902, 1996.

McMurry, P. H., Takano, H., and Anderson, G. R.: Study of the ammonia (gas)-sulfuric acid (aerosol) reaction rate, Environ. Sci. Technol., 17, 347-352, 1983.

McMurry, P. H.: A review of atmospheric aerosol measurements, Atmospheric Environment, 34(12-14), 1959-1999, 2000.

Mejia, J. F., and Morawska, L.: An investigation of nucleation events in a coastal urban environment in the Southern Hemisphere, Atmospheric Chemistry and Physics, 9(20), 7877-7888, 2009.

Mertes, S., Lehmann, K., Nowak, A., Massling, A., and Wiedensohler, A.: Link between aerosol hygroscopic growth and droplet activation observed for hill-capped clouds at connected flow conditions during FEBUKO, Atmospheric Environment, 39(23-24), 4247-4256, 10.1016/j.atmosenv.2005.02.010, 2005.

Meskhidze, N., and Nenes, A.: Phytoplankton and cloudiness in the Southern Ocean, Science, 314(5804), 1419-1423, 10.1126/science.1131779, 2006.

Meyer, N. K., and Ristovski, Z. D.: Ternary Nucleation as a Mechanism for the Production of Diesel Nanoparticles: Experimental Analysis of the Volatile and Hygroscopic Properties of Diesel Exhaust Using the Volatilization and Humidification Tandem Differential Mobility Analyzer, Environ. Sci. Tech., 41(21), 7309-7314, 10.1021/es062574v, 2007.

Meyer, N. K., Duplissy, J., Gysel, M., Metzger, A., Dommen, J., Weingartner, E., Alfarra, M. R., Prevot, A. S. H., Fletcher, C., Good, N., McFiggans, G., Jonsson, A. M., Hallquist, M., Baltensperger, U., and Ristovski, Z. D.: Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and unseeded SOA particles, Atmospheric Chemistry and Physics, 9(2), 721-732, 2009.

Middlebrook, A. M., Murphy, D. M., and Thomson, D. S.: Observations of organic material in individual marine particles at Cape Grim during the First Aerosol Characterization Experiment (ACE 1), J. Geophys. Res., 103(D13), 16475-16483, 10.1029/97jd03719, 1998.

Mikhailov, E., Vlasenko, S., Niessner, R., and Poschl, U.: Interaction of aerosol particles composed of protein and salts with water vapor: hygroscopic growth and microstructural rearrangement, Atmospheric Chemistry and Physics, 4, 323-350, 2004.

Ming, Y., and Russell, L. M.: Predicted hygroscopic growth of sea salt aerosol, J. Geophys. Res., 106 (D22), 28259-28274, 2001.

Ming, Y., and Russell, L. M.: Thermodynamic equilibrium of organic-electrolyte mixtures in aerosol particles, Aiche J., 48(6), 1331-1348, 2002.

Mircea, M., Facchini, M. C., Decesari, S., Fuzzi, S., and Charlson, R. J.: The influence of the organic aerosol component on CCN supersaturation spectra for different aerosol types, Tellus Series B, 54(1), 74-81, 2002.

Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., and Suzuki, K.: Fatty acids in the marine atmosphere: Factors governing their concentrations and evaluation of organic films on sea-salt particles, J. Geophys. Res., 107(D17), 4325, 10.1029/2001jd001278, 2002.

Modini, R. L., Ristovski, Z. D., Johnson, G. R., He, C., Surawski, N., Morawska, L., Suni, T., and Kulmala, M.: New particle formation and growth at a remote, sub-tropical coastal location, Atmospheric Chemistry and Physics, 9(19), 7607-7621, 2009.

Modini, R. L., Harris, B., and Ristovski, Z. D.: The organic fraction of bubble-generated, accumulation mode Sea Spray Aerosol (SSA), Atmospheric Chemistry and Physics, 10(6), 2867-2877, 2010a.

Modini, R. L., Johnson, G. R., He, C., and Ristovski, Z. D.: Observation of the suppression of water uptake by marine particles, Atmospheric Research, In Press, Corrected Proof, 2010b.

Monahan, E. C., and Muircheartaigh, I.: Optimal power-law description of oceanic whiecap coverage dependence on wind speed, Journal of Physical Oceanography, 10, 2094-2099, 1980.

Moore, R. H., Ingall, E. D., Sorooshian, A., and Nenes, A.: Molar mass, surface tension, and droplet growth kinetics of marine organics from measurements of CCN activity, Geophys. Res. Lett., 35, L07801, 10.1029/2008gl033350, 2008.

Mukai, H., Yokouchi, Y., and Suzuki, M.: Seasonal-variation of methanesulfonic-acid in the atmosphere over the Oki Islands in the Sea of Japan, Atmospheric Environment, 29(14), 1637-1648, 1995.

Muller, C., Iinuma, Y., Karstensen, J., van Pinxteren, D., Lehmann, S., Gnauk, T., and Herrmann, H.: Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands, Atmospheric Chemistry and Physics, 9(24), 9587-9597, 2009.

Muller, K., Lehmann, S., van Pinxteren, D., Gnauk, T., Niedermeier, N., Wiedensohler, A., and Herrmann, H.: Particle characterization at the Cape Verde atmospheric observatory during the 2007 RHaMBLe intensive, Atmospheric Chemistry and Physics, 10(6), 2709-2721, 2010.

Murphy, D. M., Anderson, J. R., Quinn, P. K., McInnes, L. M., Brechtel, F. J., Kreidenweis, S. M., Middlebrook, A. M., Posfai, M., Thomson, D. S., and Buseck, P. R.: Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer, Nature, 392, 62-65, 1998.

Nenes, A., Ghan, S., Abdul-Razzak, H., Chuang, P. Y., and Seinfeld, J. H.: Kinetic limitations on cloud droplet formation and impact on cloud albedo, Tellus Series B, 53(2), 133-149, 2001.

Niedermeier, D., Wex, H., Voigtländer, J., Stratmann, F., Brüggemann, E., Kiselev, A., Henk, H., and Heintzenberg, J.: LACIS-measurements and parameterization of sea-salt particle hygroscopic growth and activation, Atmos. Chem. Phys., 8(3), 579-590, 2008.

Nilsson, E., Swietlicki, E., Sjogren, S., Löndahl, J., Nyman, M., and Svenningsson, B.: Development of an H-TDMA for long-term unattended measurement of the hygroscopic properties of atmospheric aerosol particles, Atmospheric Measurement Techniques, 2(1), 313 - 318, 2009.

Nilsson, E. D., Martensson, E. M., Van Ekeren, J. S., De Leeuw, G., Moerman, M., and O'Dowd, C.: Primary marine aerosol emissions: size resolved eddy covariance measurements with estimates of the sea salt and organic carbon fractions, Atmospheric Chemistry and Physics Discussions, 7, 13345-13400, 2007.

Novakov, T., Corrigan, C. E., Penner, J. E., Chuang, C. C., Rosario, O., and Bracero, O. L. M.: Organic aerosols in the Caribbean trade winds: A natural source?, J. Geophys. Res., 102(D17), 21307-21313, 10.1029/97jd01487, 1997.

O'Dowd, C., Smith, M. H., Consterdine, I. E., and Lowe, J. A.: Marine aerosol, sea salt, and the marine sulphur cycle: a short review, Atmospheric Environment, 31(1), 73-80, 1997.

O'Dowd, C. D., and Smith, M. H.: Physiochemical properties of aerosols over the Northeast Atlantic: Evidence for wind-speed-related submicron sea-salt aerosol production, Journal of Geophysical Research, 98(D1), 1137-1149, 1993.

O'Dowd, C. D., Lowe, J. A., Smith, M. H., and Kaye, A. D.: The relative importance of non-sea-salt sulphate and sea-salt aerosol to the marine cloud condensation nuclei population: An improved multi-component aerosol-cloud droplet parametrization, Q. J. R. Meteorol. Soc., 125(556), 1295-1313, 1999.

O'Dowd, C. D., Hämeri, K., Mäkelä, J., Väkeva, M., Aalto, P., de Leeuw, G., Kunz, G. J., Becker, E., Hansson, H.-C., Allen, A. G., Harrison, R. M., Berresheim, H., Kleefeld, C., Geever, M., Jennings, S. G., and Kulmala, M.: Coastal new particle formation: Environmental conditions and aerosol physicochemical characteristics during nucleation bursts, J. Geophys. Res., 107(D19), 8107, 10.1029/2000jd000206, 2002a.

O'Dowd, C. D., Hämeri, K., Mäkelä, J. M., Pirjola, L., Kulmala, M., Jennings, S. G., Berresheim, H., Hansson, H.-C., de Leeuw, G., Kunz, G. J., Allen, A. G., Hewitt, C. N., Jackson, A., Viisanen, Y., and Hoffmann, T.: A dedicated study of New Particle Formation and Fate in the Coastal Environment (PARFORCE): Overview of objectives and achievements, J. Geophys. Res., 107(D19), 8108, 10.1029/2001jd000555, 2002b.

O'Dowd, C. D., Jimenez, J. L., Bahreini, R., Flagan, R. C., Seinfeld, J. H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S. G., and Hoffmann, T.: Marine aerosol formation from biogenic iodine emissions, Nature, 417(6889), 632-636, 2002c.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J.-P.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676-680, 2004.

O'Dowd, C. D., and Hoffmann, T.: Coastal New Particle Formation: A Review of the Current State-Of-The-Art, Environmental Chemistry, 2, 245-255, 2005.

O'Dowd, C. D., Jimenez, J. L., Bahreini, R., Flagan, R. C., Seinfeld, J. H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S. G., and Hoffmann, T.: Marine aerosols and iodine emissions - Reply, Nature, 433(7026), E13-E14, 10.1038/nature03373, 2005.

O'Dowd, C. D., and De Leeuw, G.: Marine aerosol production: a review of the current knowledge, Philos. Trans. R. Soc. A-Math. Phys. Eng. Sci., 365, 1753-1774, 10.1098/rsta.2007.2043, 2007.

O'Dowd, C. D., Langmann, B., Varghese, S., Scannell, C., Ceburnis, D., and Facchini, M. C.: A combined organic-inorganic sea-spray source function, Geophys. Res. Lett., 35(1), L01801, 10.1029/2007gl030331, 2008.

Oppo, C., Bellandi, S., Degli Innocenti, N., Stortini, A. M., Loglio, G., Schiavuta, E., and Cini, R.: Surfactant components of marine organic matter as agents for biogeochemical fractionation and pollutant transport via marine aerosols, Mar. Chem., 63(3-4), 235-253, 1999.

Orsini, D. A., Wiedensohler, A., Stratmann, F., and Covert, D. S.: A new volatility tandem differential mobility analyzer to measure the volatile sulfuric acid aerosol fraction, J. Atmos. Ocean. Technol., 16(6), 760-772, 1999.

Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C., and Brown, S. S.: High levels of nitryl chloride in the polluted subtropical marine boundary layer, Nat. Geosci., 1, 324-328, 10.1038/ngeo177, 2008.

Ovadnevaite, J., Ceburnis, D., Plauskaite-Sukiene, K., Modini, R., Dupuy, R., Rimselyte, I., Ramonet, M., Kvietkus, K., Ristovski, Z., Berresheim, H., and O'Dowd, C. D.: Volcanic sulphate and arctic dust plumes over the North Atlantic Ocean, Atmospheric Environment, 43(32), 4968-4974, 2009.

Parsons, M. T., Knopf, D. A., and Bertram, A. K.: Deliquescence and crystallization of ammonium sulfate particles internally mixed with water-soluble organic compounds, J. Phys. Chem. A, 108(52), 11600-11608, 10.1021/jp0462862, 2004.

Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions, Environ. Sci. Technol., 35(22), 4495-4501, 10.1021/es0107531, 2001a.

Peng, C. G., Chow, A. H. L., and Chan, C. K.: Study of the hygroscopic properties of selected pharmaceutical aerosols using single particle levitation, Pharm. Res., 17(9), 1104-1109, 2000.

Peng, C. G., and Chan, C. K.: The water cycles of water-soluble organic salts of atmospheric importance, Atmospheric Environment, 35(7), 1183-1192, 2001.

Peng, C. G., Chow, A. H. L., and Chan, C. K.: Hygroscopic study of glucose, citric acid, and sorbitol using an electrodynamic balance: Comparison with UNIFAC predictions, Aerosol Sci. Technol., 35(3), 753-758, 2001b.

Perry, K. D., and Hobbs, P. V.: Further evidence for particle nucleation in clear air adjacent to marine cumulus clouds, J. Geophys. Res., 99, 22,803–822,818, 1994.

Peterson, R. E., and Tyler, B. J.: Analysis of organic and inorganic species on the surface of atmospheric aerosol using time-of-flight secondary ion mass spectrometry (TOF-SIMS), Atmospheric Environment, 36(39-40), 6041-6049, 2002.

Petters, M. D., and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmospheric Chemistry and Physics, 7(8), 1961-1971, 2007.

Petters, M. D., and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity - Part 2: Including solubility, Atmospheric Chemistry and Physics, 8(20), 6273-6279, 2008.

Pierce, J. R., and Adams, P. J.: Global evaluation of CCN formation by direct emission of sea salt and growth of ultrafine sea salt, Journal of Geophysical Research, 111, D06203, doi:10.1029/2005JD006186, 2006.

Pirjola, L., O'Dowd, C. D., Brooks, I. M., and Kulmala, M.: Can new particle formation occur in the clean marine boundary layer?, J. Geophys. Res., 105(D21), 26531-26546, 10.1029/2000jd900310, 2000.

Pirjola, L., O'Dowd, C. D., Yoon, Y. J., and Sellegri, K.: Modelling iodine particle formation and growth from seaweed in a chamber, Environmental Chemistry, 2(4), 271-281, 10.1071/en05075, 2005.

Plauskaite, K., Ulevicius, V., Spirkauskaite, N., Bycenkiene, S., Zielinski, T., Petelski, T., and Ponczkowska, A.: Observations of new particle formation events in the south-eastern Baltic Sea, Oceanologia, 52(1), 53-75, 2010.

Pope, C. A., and Dockery, D. W.: Health effects of fine particulate air pollution: Lines that connect, J. Air Waste Manage. Assoc., 56, 709-742, 2006.

Pope, F. D., Dennis-Smither, B. J., Griffiths, P. T., Clegg, S. L., and Cox, R. A.: Studies of Single Aerosol Particles Containing Malonic Acid, Glutaric Acid, and Their Mixtures with Sodium Chloride. I. Hygroscopic Growth, J. Phys. Chem. A, 114(16), 5335-5341, 10.1021/jp100059k, 2010.

Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E., Russell, L. M., and Ming, Y.: The effects of low molecular weight dicarboxylic acids on cloud formation, J. Phys. Chem. A, 105(50), 11240-11248, 10.1021/jp012427d, 2001.

Prenni, A. J., De Mott, P. J., and Kreidenweis, S. M.: Water uptake of internally mixed particles containing ammonium sulfate and dicarboxylic acids, Atmospheric Environment, 37(30), 4243-4251, 10.1016/s1352-2310(03)00559-4, 2003.

Putaud, J. P., Van Dingenen, R., Mangoni, M., Virkkula, A., Raes, F., Maring, H., Prospero, J. M., Swietlicki, E., Berg, O. H., Hillamo, R., and Makela, T.: Chemical mass closure and assessment of the origin of the submicron aerosol in the marine boundary layer and the free troposphere at Tenerife during ACE-2, Tellus Series B, 52(2), 141-168, 2000.

Quinn, P. K., Kapustin, V. N., Bates, T. S., and Covert, D. S.: Chemical and optical properties of marine boundary layer aerosol particles of the mid-Pacific in relation to sources and meteorological transport, Journal of Geophysical Research, 101(D3), 6931-6951, 1996.

Quinn, P. K., and Coffman, D. J.: Comment on "Contribution of different aerosol species to the global aerosol extinction optical thickness: Estimates from model results" by Tegen et al, J. Geophys. Res., 104(D4), 4241-4248, 10.1029/1998jd200066, 1999.

Quinn, P. K., Bates, T. S., Miller, T. L., Coffman, D. J., Johnson, J. E., Harris, J. M., Ogren, J. A., Forbes, G., Anderson, T. L., Covert, D. S., and Rood, M. J.: Surface submicron aerosol chemical composition: What fraction is not sulfate?, J. Geophys. Res., 105(D5), 6785-6805, 10.1029/1999jd901034, 2000.

Quinn, P. K., and Bates, T. S.: Regional aerosol properties: Comparisons of boundary layer measurements from ACE 1, ACE 2, aerosols99, INDOEX, ACE asia, TARFOX, and NEAQS, Journal of Geophysical Research, 110 (D14), 24, D14202 10.1029/2004jd004755, 2005.

Raatikainen, T., and Laaksonen, A.: Application of several activity coefficient models to water-organic-electrolyte aerosols of atmospheric interest, Atmospheric Chemistry and Physics, 5, 2475-2495, 2005.

Rader, D. J., and McMurry, P. H.: Application of the tandem differential mobility analyzer to studies of droplet growth or evaporation, J. Aerosol. Sci., 17(5), 771-787, 1986.

Raes, F.: Entrainment of free tropospheric aerosols as a regulating mechanism for cloud condensation nuclei in the remote marine boundary layer, J. Geophys. Res., 100(D2), 2893-2903, 10.1029/94jd02832, 1995.

Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Atmosphere - Aerosols, climate, and the hydrological cycle, Science, 294, 2119-2124, 2001.

Randles, C. A., Russell, L. M., and Ramaswamy, V.: Hygroscopic and optical properties of organic sea salt aerosol and consequences for climate forcing, Geophys. Res. Lett., 31, L16108, doi:10.1029/2004GL020628, 2004.

Rinaldi, M., Decesari, S., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., O'Dowd, C., Ceburnis, D., and Facchini, M. C.: Primary and secondary organic marine aerosol and oceanic biological activity: recent results and new perspectives for future studies, Advances in Meteorology, In press, 2010.

Rissler, J., Swietlicki, E., Zhou, J., Roberts, G., Andreae, M. O., Gatti, L. V., and Artaxo, P.: Physical properties of the sub-micrometer aerosol over the Amazon rain forest during the wet-to-dry season transition - comparison of modeled and measured CCN concentrations, Atmospheric Chemistry and Physics, 4, 2119-2143, 2004.

Rissler, J., Vestin, A., Swietlicki, E., Fisch, G., Zhou, J., Artaxo, P., and Andreae, M. O.: Size distribution and hygroscopic properties of aerosol particles from dry-season biomass burning in Amazonia, Atmospheric Chemistry and Physics, 6, 471-491, 2006.

Rissman, T. A., Varutbangkul, V., Surratt, J. D., Topping, D. O., McFiggans, G., Flagan, R. C., and Seinfeld, J. H.: Cloud condensation nucleus (CCN) behavior of organic aerosol particles generated by atomization of water and methanol solutions, Atmospheric Chemistry and Physics, 7(11), 2949-2971, 2007.

Ristovski, Z. D., Fletcher, C., D’Anna, B., Johnson, G. R., and Bostrom, J. T.: Characterization of iodine particles with Volatilization-Humidification Tandem Differential Mobility Analyser (VH-TDMA), Raman and SEM techniques, Atmos. Chem. Phys. Discuss., 6(1), 1481-1508, 2006.

Ristovski, Z. D., Suni, T., Kulmala, M., Boy, M., Meyer, N. K., Duplissy, J., Turnipseed, A., Morawska, L., and Baltensperger, U.: The role of sulphates and organic vapours in growth of newly formed particles in a eucalypt forest, Atmospheric Chemistry and Physics, 10 (6), 2919-2926, 2010.

Roberts, G. C., Day, D. A., Russell, L. M., Dunlea, E. J., Jimenez, J. L., Tomlinson, J. M., Collins, D. R., Shinozuka, Y., and Clarke, A. D.: Characterization of particle cloud droplet activity and composition in the free troposphere and the boundary layer during INTEX-B, Atmospheric Chemistry and Physics Discussions, 10(2), 3499 - 3546, 2010.

Rodriguez, S., Cuevas, E., Gonzalez, Y., Ramos, R., Romero, P. M., Perez, N., Querol, X., and Alastuey, A.: Influence of sea breeze circulation and road traffic emissions on the relationship between particle number, black carbon, PM1, PM2.5 and PM2.5-10 concentrations in a coastal city, Atmospheric Environment, 42(26), 6523-6534, 10.1016/j.atmosenv.2008.04.022, 2008.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Poschl, U.: Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, Atmospheric Chemistry and Physics, 8(5), 1153-1179, 2008.

Ruehl, C. R., Chuang, P. Y., and Nenes, A.: How quickly do cloud droplets form on atmospheric particles?, Atmospheric Chemistry and Physics, 8(4), 1043-1055, 2008.

Ruehl, C. R., Chuang, P. Y., and Nenes, A.: Distinct CCN activation kinetics above the marine boundary layer along the California coast, Geophys. Res. Lett., 36(15), L15814, 10.1029/2009gl038839, 2009.

Russell, L. M., Maria, S. F., and Myneni, S. C. B.: Mapping organic coatings on atmospheric particles, Geophysical Research Letters, 29(16), 4, 177910.1029/2002gl014874, 2002.

Russell, L. M., Mensah, A. A., Fischer, E. V., Sive, B. C., Varner, R. K., Keene, W. C., Stutz, J., and Pszenny, A. A. P.: Nanoparticle growth following photochemical alpha and beta-pinene oxidation at Appledore Island during International Consortium for Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals 2004, J. Geophys. Res., 112(D10), D10S21, 10.1029/2006jd007736, 2007.

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, Proc. Natl. Acad. Sci. U. S. A., 107(15), 6652-6657, 10.1073/pnas.0908905107, 2010.

Saiz-Lopez, A., Saunders, R. W., Joseph, D. M., Ashworth, S. H., and Plane, J. M. C.: Absolute absorption cross-section and photolysis rate of I-2, Atmospheric Chemistry and Physics, 4, 1443-1450, 2004.

Saiz-Lopez, A., Plane, J. M. C., McFiggans, G., Williams, P. I., Ball, S. M., Bitter, M., Jones, R. L., Hongwei, C., and Hoffmann, T.: Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation, Atmospheric Chemistry and Physics, 6, 883-895, 2006.

Savoie, D. L., Arimoto, R., Keene, W. C., Prospero, J. M., Duce, R. A., and Galloway, J. N.: Marine biogenic and anthropogenic contributions to non-sea-salt sulfate in the marine boundary layer over the North Atlantic Ocean, J. Geophys. Res., 107(D18), 4356, 10.1029/2001jd000970, 2002.

Saxena, P., Hildemann, L. M., McMurry, P. H., and Seinfeld, J. H.: Organics alter hygroscopic behavior of atmospheric particles, J. Geophys. Res., 100(D9), 18755-18770, 10.1029/95jd01835, 1995.

Schwartz, S. E.: The Whitehouse effect - Shortwave radiative forcing of climate by anthropogenic aerosols: An overview, J. Aerosol. Sci., 27(3), 359-382, 1996.

Sciare, J., Kanakidou, M., and Mihalopoulos, N.: Diurnal and seasonal variation of atmospheric dimethylsulfoxide at Amsterdam Island in the southern Indian Ocean, J. Geophys. Res., 105(D13), 17257-17265, 10.1029/1999jd901186, 2000a.

Sciare, J., Mihalopoulos, N., and Dentener, F. J.: Interannual variability of atmospheric dimethylsulfide in the southern Indian Ocean, J. Geophys. Res., 105(D21), 26369-26377, 10.1029/2000jd900236, 2000b.

Sciare, J., Favez, O., Sarda-Estève, R., Oikonomou, K., Cachier, H., and Kazan, V.: Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source, J. Geophys. Res., 114(D15), D15302, 10.1029/2009jd011998, 2009.

Seidl, W.: Model for a surface film of fatty acids on rain water and aerosol particles, Atmospheric Environment, 34(28), 4917-4932, 2000.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: From air pollution to climate change, John Wiley & Sons, Inc. , New York, 1998.

Sellegri, K., O'Dowd, C. D., Yoon, Y. J., Jennings, S. G., and de Leeuw, G.: Surfactants and submicron sea spray generation, J. Geophys. Res., 111, D22215, doi:10.1029/2005JD006658, 2006.

Sellegri, K., Villani, P., Picard, D., Dupuy, R., O'Dowd, C., and Laj, P.: Role of the volatile fraction of submicron marine aerosol on its hygroscopic properties, Atmospheric Research, 90(2-4), 272-277, 10.1016/j.atmosres.2008.04.004, 2008.

Shantz, N. C., Chang, R. Y. W., Slowik, J. G., Vlasenko, A., Abbatt, J. P. D., and Leaitch, W. R.: Slower CCN growth kinetics of anthropogenic aerosol compared to biogenic aerosol observed at a rural site, Atmospheric Chemistry and Physics, 10(1), 299-312, 2010.

Shulman, M. L., Jacobson, M. C., Charlson, R. J., Synovec, R. E., and Young, T. E.: Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets, Geophys. Res. Lett., 23(3), 277-280, 1996.

Sievering, H., Boatman, J., Gorman, E., Kim, Y., Anderson, L., Ennis, G., Luria, M., and Pandis, S.: Removal of sulphur from the marine boundary layer by ozone oxidation in sea-salt aerosols Nature, 360(6404), 571-573, 1992.

Sievering, H., Cainey, J., Harvey, M., McGregor, J., Nichol, S., and Quinn, P.: Aerosol non-sea-salt sulfate in the remote marine boundary layer under clear-sky and normal cloudiness conditions: Ocean-derived biogenic alkalinity enhances sea-salt sulfate production by ozone oxidation, J. Geophys. Res., 109(D19), D19317, 10.1029/2003jd004315, 2004.

Sjogren, S., Gysel, M., Weingartner, E., Baltensperger, U., Cubison, M. J., Coe, H., Zardini, A. A., Marcolli, C., Krieger, U. K., and Peter, T.: Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures, J. Aerosol. Sci., 38(2), 157-171, 10.1016/j.jaerosci.2006.11.005, 2007.

Smoydzin, L., and von Glasow, R.: Do organic surface films on sea salt aerosols influence atmospheric chemistry? a model study, Atmospheric Chemistry and Physics, 7(21), 5555-5567, 2007.

Snead, C. C., and Zung, J. T.: The effects of insoluble films upon the evaporation kinetics of liquid droplets, Journal of Colloid and Interface Science, 27(1), 25-31, 1968.

Sorjamaa, R., Svenningsson, B., Raatikainen, T., Henning, S., Bilde, M., and Laaksonen, A.: The role of surfactants in Kohler theory reconsidered, Atmospheric Chemistry and Physics, 4, 2107-2117, 2004.

Sorjamaa, R., and Laaksonen, A.: The influence of surfactant properties on critical supersaturations of cloud condensation nuclei, J. Aerosol. Sci., 37(12), 1730-1736, 10.1016/j.jaerosci.2006.07.004, 2006.

Sorooshian, A., Padró, L. T., Nenes, A., Feingold, G., McComiskey, A., Hersey, S. P., Gates, H., Jonsson, H. H., Miller, S. D., Stephens, G. L., Flagan, R. C., and Seinfeld, J. H.: On the link between ocean biota emissions, aerosol, and maritime clouds: Airborne, ground, and satellite measurements off the coast of California, Global Biogeochem. Cycles, 23(4), GB4007, 10.1029/2009gb003464, 2009.

Spiel, D. E.: On the births of jet drops from bubbles bursting on water surfaces, J. Geophys. Res., 100(C3), 4995-5006, 1995.

Spiel, D. E.: On the births of film drops from bubbles bursting on seawater surfaces, J. Geophys. Res., 103(C11), 24907-24918, 1998.

Stokes, R. H., and Robinson, R. A.: Interactions in Aqueous Nonelectrolyte Solutions. I. Solute-Solvent Equilibria, J. Phys. Chem., 70(7), 2126-2131, 1966.

Stratmann, F., Kiselev, A., Wurzler, S., Wendisch, M., Heintzenberg, J., Charlson, R. J., Diehl, K., Wex, H., and Schmidt, S.: Laboratory studies and numerical simulations of cloud droplet formation under realistic supersaturation conditions, J. Atmos. Ocean. Technol., 21(6), 876-887, 2004.

Strom, J., Engvall, A. C., Delbart, F., Krejci, R., and Treffeisen, R.: On small particles in the Arctic summer boundary layer: observations at two different heights near Ny-Alesund, Svalbard, Tellus Series B, 61(2), 473-482, 10.1111/j.1600-0889.2008.00412.x, 2009.

Stuhlman, O.: The mechanics of effervescence, Physics, 2, 457-466, 1932.

Svenningsson, B., Hansson, H. C., Wiedensohler, A., Noone, K., Ogren, J., Hallberg, A., and Colvile, R.: Hygroscopic growth of aerosol particles and its influence on nucleation scavenging in cloud: Experimental results from Kleiner Feldberg, Journal of Atmospheric Chemistry, 19(1-2), 129-152, 1994.

Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S., Zhou, J., Monster, J., and Rosenorn, T.: Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance, Atmospheric Chemistry and Physics, 6, 1937-1952, 2006.

Svenningsson, I. B., Hansson, H. C., Wiedensohler, A., Ogren, J. A., Noone, K. J., and Hallberg, A.: Hygroscopic growth of aerosol particles in the Po Valley, Tellus Series B, 44(5), 556-569, 1992.

Swietlicki, E., Zhou, J. C., Berg, O. H., Martinsson, B. G., Frank, G., Cederfelt, S. I., Dusek, U., Berner, A., Birmili, W., Wiedensohler, A., Yuskiewicz, B., and Bower, K. N.: A closure study of sub-micrometer aerosol particle hygroscopic behaviour, Atmospheric Research, 50(3-4), 205-240, 1999.

Swietlicki, E., Zhou, J. C., Covert, D. S., Hameri, K., Busch, B., Vakeva, M., Dusek, U., Berg, O. H., Wiedensohler, A., Aalto, P., Makela, J., Martinsson, B. G., Papaspiropoulos, G., Mentes, B., Frank, G., and Stratmann, F.: Hygroscopic properties of aerosol particles in the northeastern Atlantic during ACE-2, Tellus Series B, 52(2), 201-227, 2000.

Swietlicki, E., Hansson, H. C., Hameri, K., Svenningsson, B., Massling, A., McFiggans, G., McMurry, P. H., Petaja, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., and Kulmala, M.: Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments - a review, Tellus Series B, 60(3), 432-469, 10.1111/j.1600-0889.2008.00350.x, 2008.

Takahama, S., Pathak, R. K., and Pandis, S. N.: Efflorescence transitions of ammonium sulfate particles coated with secondary organic aerosol, Environ. Sci. Technol., 41(7), 2289-2295, 10.1021/es0619915, 2007.

Tang, I. N., and Munkelwitz, H. R.: Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance, J. Geophys. Res., 99(D9), 18801-18808, 10.1029/94jd01345, 1994.

Tang, I. N.: Chemical and size effects of hygroscopic aerosols on light scattering coefficients, J. Geophys. Res., 101(D14), 19245-19250, 10.1029/96jd03003, 1996.

Tang, I. N., Tridico, A. C., and Fung, K. H.: Thermodynamic and optical properties of sea salt aerosols, J. Geophys. Res., 102(D19), 23269-23275, 10.1029/97jd01806, 1997.

Tervahattu, H., Hartonen, K., Kerminen, V.-M., Kupiainen, K., Aarnio, P., Koskentalo, T., Tuck, A. F., and Vaida, V.: New evidence of an organic layer on marine aerosols, J. Geophys. Res., 107(D7), 4053, 10.1029/2000jd000282, 2002.

Tervahattu, H., Juhanoja, J., Vaida, V., Tuck, A. F., Niemi, J. V., Kupiainen, K., Kulmala, M., and Vehkamäki, H.: Fatty acids on continental sulfate aerosol particles, J. Geophys. Res., 110(D6), D06207, 10.1029/2004jd005400, 2005.

Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dube, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, Nature, 464 (7286), 271-274, 10.1038/nature08905, 2010.

Tomlinson, J. M., Li, R., and Collins, D. R.: Physical and chemical properties of the aerosol within the southeastern Pacific marine boundary layer, J. Geophys. Res., 112(D12), D12211, 10.1029/2006jd007771, 2007.

Tong, C. H., Clegg, S. L., and Seinfeld, J. H.: Comparison of activity coefficient models for atmospheric aerosols containing mixtures of electrolytes, organics, and water, Atmospheric Environment, 42(21), 5459-5482, 10.1016/j.atmosenv.2008.02.040, 2008.

Topping, D. O., McFiggans, G. B., and Coe, H.: A curved multi-component aerosol hygroscopicity model framework: Part 1 - Inorganic compounds, Atmospheric Chemistry and Physics, 5, 1205-1222, 2005a.

Topping, D. O., McFiggans, G. B., and Coe, H.: A curved multi-component aerosol hygroscopicity model framework: Part 2 - Including organic compounds, Atmospheric Chemistry and Physics, 5, 1223-1242, 2005b.

Topping, D. O., McFiggans, G. B., Kiss, G., Varga, Z., Facchini, M. C., Decesari, S., and Mircea, M.: Surface tensions of multi-component mixed inorganic/organic aqueous systems of atmospheric significance: measurements, model predictions and importance for cloud activation predictions, Atmospheric Chemistry and Physics, 7(9), 2371-2398, 2007.

Twomey, S.: Pollution and the planetary albedo, Atmospheric Environment, 8, 1251-1256, 1974.

Tyree, C. A., Hellion, V. M., Alexandrova, O. A., and Allen, J. O.: Foam droplets generated from natural and artificial seawaters, J. Geophys. Res., 112, D12204, doi:10.1029/2006JD007729, 2007.

Ulevicius, V., Mordas, G., and Plauskaite, K.: Evolution of aerosol particle size distribution in the coastal environment: effect of relative humidity, SO_2 and NO_2, Environ. Chem. Phys., 24(1), 13-17, 2002.

Vaattovaara, P., Huttunen, P. E., Yoon, Y. J., Joutsensaari, J., Lehtinen, K. E. J., O'Dowd, C. D., and Laaksonen, A.: The composition of nucleation and Aitken modes particles during coastal nucleation events: evidence for marine secondary organic contribution, Atmos. Chem. Phys., 6(12), 4601-4616, 2006.

Väkevä, M., Hämeri, K., and Aalto, P. P.: Hygroscopic properties of nucleation mode and Aitken mode particles during nucleation bursts and in background air on the west coast of Ireland, J. Geophys. Res., 107(D19), 8104, 10.1029/2000jd000176, 2002.

Van Dingenen, R., Raes, F., Putaud, J.-P., Virkkula, A., and Mangoni, M.: Processes determining the relationship between aerosol number and non-sea-salt sulfate mass concentrations in the clean and perturbed marine boundary layer, J. Geophys. Res., 104(D7), 8027-8038, 10.1029/1998jd100059, 1999.

Varutbangkul, V., Brechtel, F. J., Bahreini, R., Ng, N. L., Keywood, M. D., Kroll, J. H., Flagan, R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Hygroscopicity of secondary organic aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds, Atmospheric Chemistry and Physics, 6, 2367-2388, 2006.

Vignati, E., de Leeuw, G., and Berkowicz, R.: Modeling coastal aerosol transport and effects of surf-produced aerosols on processes in the marine atmospheric boundary layer, J. Geophys. Res., 106(D17), 20225-20238, 10.1029/2000jd000025, 2001.

Vignati, E., Facchini, M. C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou, M., Myriokefalitakis, S., Dentener, F., and O'Dowd, C. D.: Global scale emission and distribution of sea-spray aerosol: Sea-salt and organic enrichment, Atmospheric Environment, 44(5), 670-677, 10.1016/j.atmosenv.2009.11.013, 2010.

Villani, P., Picard, D., Michaud, V., Laj, P., and Wiedensohler, A.: Design and validation of a volatility hygroscopic tandem differential mobility analyzer (VH-TDMA) to characterize the relationships between the thermal and hygroscopic properties of atmospheric aerosol particles, Aerosol Sci. Technol., 42(9), 729-741, 10.1080/02786820802255668, 2008.

Villani, P., Sellegri, K., Monier, M., and Laj, P.: Influence of semi-volatile species on particle hygroscopic growth, Atmospheric Chemistry and Physics Discussions, 9(1), 2021-2047, 2009.

von Glasow, R., and Crutzen, P. J.: Model study of multiphase DMS oxidation with a focus on halogens, Atmospheric Chemistry and Physics, 4, 589-608, 2004.

von Glasow, R., Bobrowski, N., and Kern, C.: The effects of volcanic eruptions on atmospheric chemistry, Chem. Geol., 263(1-4), 131-142, 10.1016/j.chemgeo.2008.08.020, 2009.

Wang, H. B., Kawamura, K., and Yamazaki, K.: Water-soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and western Pacific Ocean, Journal of Atmospheric Chemistry, 53(1), 43-61, 10.1007/s10874-006-1479-4, 2006.

Weingartner, E., Gysel, M., and Baltensperger, U.: Hygroscopicity of aerosol particles at low temperatures. 1. New low-temperature H-TDMA instrument: Setup and first applications, Environ. Sci. Technol., 36(1), 55-62, 10.1021/es010054o, 2002.

Wen, J., Zhao, Y., and Wexler, A. S.: Marine particle nucleation: Observation at Bodega Bay, California, J. Geophys. Res., 111(D8), D08207, 10.1029/2005jd006210, 2006.

Wex, H., Hennig, T., Salma, I., Ocskay, R., Kiselev, A., Henning, S., Massling, A., Wiedensohler, A., and Stratmann, F.: Hygroscopic growth and measured and modeled critical super-saturations of an atmospheric HULIS sample, Geophys. Res. Lett., 34(2), L02818, 10.1029/2006gl028260, 2007.

Wex, H., Stratmann, F., Topping, D., and McFiggans, G.: The Kelvin versus the Raoult Term in the Kohler Equation, J. Atmos. Sci., 65(12), 4004-4016, 10.1175/2008jas2720.1, 2008.

Wex, H., Petters, M. D., Carrico, C. M., Hallbauer, E., Massling, A., McMeeking, G. R., Poulain, L., Wu, Z., Kreidenweis, S. M., and Stratmann, F.: Towards closing the gap between hygroscopic growth and activation for secondary organic aerosol: Part 1-Evidence from measurements, Atmospheric Chemistry and Physics, 9(12), 3987-3997, 2009.

Wise, M. E., Surratt, J. D., Curtis, D. B., Shilling, J. E., and Tolbert, M. A.: Hygroscopic growth of ammonium sulfate/dicarboxylic acids, J. Geophys. Res., 108(D20), 4638, 10.1029/2003jd003775, 2003.

Wise, M. E., Biskos, G., Martin, S. T., Russell, L. M., and Buseck, P. R.: Phase transitions of single salt particles studied using a transmission electron microscope with an environmental cell, Aerosol Sci. Technol., 39(9), 849-856, 10.1080/02786820500295263, 2005.

Wise, M. E., Freney, E. J., Tyree, C. A., Allen, J. O., Martin, S. T., Russell, L. M., and Buseck, P. R.: Hygroscopic behavior and liquid-layer composition of aerosol particles generated from natural and artificial seawater, J. Geophys. Res., 114, D03201, doi:10.1029/2008JD010449, 2009.

Woodcock, A. H.: Note concerning human respiratory irritation associated with high concentrations of plankton and mass mortality of marine organisms, Journal of Marine Research, 7, 56-62, 1948.

Woodcock, A. H.: Atmospheric salt particles and raindrops, Journal of Meteorology, 9, 200-212, 1952.

Woodcock, A. H.: Salt nuclei in marine air as a function of altitude and wind force, Journal of Meteorology, 10, 362-371, 1953.

Xiong, J. Q., Zhong, M., Fang, C., Chen, L. C., and Lippmann, M.: Influence of Organic Films on the Hygroscopicity of Ultrafine Sulfuric Acid Aerosol, Environ. Sci. Tech., 32(22), 3536-3541, 1998.

Yassaa, N., Peeken, I., Zollner, E., Bluhm, K., Arnold, S., Spracklen, D., and Williams, J.: Evidence for marine production of monoterpenes, Environmental Chemistry, 5(6), 391-401, 10.1071/en08047, 2008.

Yoon, Y. J., and Brimblecombe, P.: Modelling the contribution of sea salt and dimethyl sulfide derived aerosol to marine CCN, Atmospheric Chemistry and Physics, 2, 17-30, 2002.

Yoon, Y. J., Ceburnis, D., Cavalli, F., Jourdan, O., Putaud, J. P., Facchini, M. C., Decesari, S., Fuzzi, S., Sellegri, K., Jennings, S. G., and O'Dowd, C. D.: Seasonal characteristics of the physicochemical properties of North Atlantic marine atmospheric aerosols, Journal of Geophysical Research, 112, 14, D04206 10.1029/2005jd007044, 2007.

Zaizen, Y., Ikegami, M., Tsutsumi, Y., Makino, Y., Okada, K., Jensen, J., and Gras, J. L.: Number concentration and size distribution of aerosol particles in the middle troposphere over the Western Pacific Ocean, Atmos. Env., 30, 1755-1762, 1996.

Zhang, Y., Seigneur, C., Seinfeld, J. H., Jacobson, M., Clegg, S. L., and Binkowski, F. S.: A comparative review of inorganic aerosol thermodynamic equilibrium modules: similarities, differences, and their likely causes, Atmospheric Environment, 34(1), 117-137, 2000.

Zhou, J., Swietlicki, E., Berg, O. H., Aalto, P. P., Hämeri, K., Nilsson, E. D., and Leek, C.: Hygroscopic properties of aerosol particles over the central Arctic Ocean during summer, J. Geophys. Res., 106(D23), 32111-32123, 10.1029/2000jd900426, 2001.

Zhou, X., Davis, A. J., Kieber, D. J., Keene, W. C., Maben, J. R., Maring, H., Dahl, E. E., Izaguirre, M. A., Sander, R., and Smoydzyn, L.: Photochemical production of hydroxyl radical and hydroperoxides in water extracts of nascent marine aerosols produced by bursting bubbles from Sargasso seawater, Geophys. Res. Lett., 35, L20803, doi:10.1029/2008GL035418, 2008.

Ziese, M., Wex, H., Nilsson, E., Salma, I., Ocskay, R., Hennig, T., Massling, A., and Stratmann, F.: Hygroscopic growth and activation of HULIS particles: experimental data and a new iterative parameterization scheme for complex aerosol particles, Atmospheric Chemistry and Physics, 8(6), 1855-1866, 2008.

Zuend, A., Marcolli, C., Luo, B. P., and Peter, T.: A thermodynamic model of mixed organic-inorganic aerosols to predict activity coefficients, Atmospheric Chemistry and Physics, 8(16), 4559-4593, 2008.

Chapter 3: New particle formation and growth at a remote, sub-tropical coastal location

R. L. Modini[1], Z. D. Ristovski[1], G. R. Johnson[1], C. He[1], N. Surawski[1], L. Morawska[1], T. Suni[2], and M. Kulmala[2]

[1]International Laboratory for Air Quality and Health, Queensland University of Technology,
Brisbane QLD 4000, Australia

2Department of Physics, P.O. Box 64, 00014 University of Helsinki, Finland

Atmospheric Chemistry and Physics, **9(19)**, 7607-7621, 2009

Statement of joint authorship

Title: New particle formation and growth at a remote, sub-tropical coastal location

Authors: R. L. Modini, Z. D. Ristovski, G. R. Johnson, C. He, N. Surawski, L. Morawska, T. Suni, and M. Kulmala

R. L. Modini

Contributed to experimental design and scientific method; conducted field work; analysed and interpreted the data; wrote manuscript

Z. D. Ristovski

Developed experimental design and scientific method; conducted field work; assisted with interpretation of data and writing of the manuscript

G. R. Johnson

Developed experimental design and scientific method; conducted field work; reviewed manuscript

C. He

Conducted field work and reviewed manuscript

N. Surawski

Contributed to data analysis and reviewed manuscript

L. Morawska

Reviewed manuscript

T. Suni

Analysed AIS data; reviewed manuscript

M. Kulmala

Reviewed manuscript

Abstract

A month-long intensive measurement campaign was conducted in March/April 2007 at Agnes Water, a remote coastal site just south of the Great Barrier Reef on the east coast of Australia. Particle and ion size distributions were continuously measured during the campaign. Coastal nucleation events were observed in clean, marine air masses coming from the south-east on 65% of the days. The events usually began at ~10:00 local time and lasted for 1-4 hrs. They were characterised by the appearance of a nucleation mode with a peak diameter of ~10 nm. The freshly nucleated particles grew within 1-4 hrs up to sizes of 20-50 nm. The events occurred when solar intensity was high (~1000 W m^{-2}) and RH was low (~60%). Interestingly, the events were not related to tide height. The volatile and hygroscopic properties of freshly nucleated particles (17-22.5 nm), simultaneously measured with a volatility-hygroscopicity-tandem differential mobility analyser (VH-TDMA), were used to infer chemical composition. The majority of the volume of these particles was attributed to internally mixed sulphate and organic components. After ruling out coagulation as a source of significant particle growth, we conclude that the condensation of sulphate and/or organic vapours was most likely responsible for driving particle growth at sizes greater than 10 nm during the nucleation events. Although there was a possibility that the precursor vapours responsible for particle formation and growth had continental sources, on the balance of available data we would suggest that the precursors were most likely of marine/coastal origin. Furthermore, a unique and particularly strong nucleation event was observed during northerly wind. The event began early one morning (08:00) and lasted almost the entire day resulting in the production of a large number of ~80 nm particles (average modal concentration during the event was 3200 cm^{-3}). The Great Barrier Reef was the most likely source of precursor vapours responsible for this event.

Introduction

Marine aerosols have an important impact on global climate through their ability to scatter and absorb radiation and influence the microphysical properties (reflectance, lifetime, and precipitation efficiency) of clouds. The number concentration of particles in the pristine marine boundary layer (MBL) is relatively stable at around 200-500 cm^{-3}. Wet and dry deposition are continuously present sinks that act to decrease this number concentration. This implies that to maintain stable number concentration there must be natural sources of marine aerosols and particles entrained from the free troposphere continuously replenishing the number of particles in the MBL. For a detailed discussion on the sources of marine aerosol see O'Dowd and De Leeuw (2007).

This article will focus only on the secondary production of ultra-fine particles through the nucleation of low vapour pressure gases produced naturally in the MBL. The secondary production of atmospheric particles requires two (likely decoupled) processes: 1) the nucleation of stable atmospheric clusters (1-3 nm) and 2) the growth or activation of these clusters into observable aerosol particles (>3 nm) (Kulmala et al., 2000). The first particle formation step requires sufficient concentrations of a low-vapour-pressure gas (typically sulphuric acid) and water vapour to form molecular clusters. This process may be enhanced by the presence of a third vapour (e.g. ammonia, low-volatility organics) that participates in a ternary nucleation mechanism, or ions that increase the stability of molecular clusters (ion-induced nucleation). The second step of particle growth to observable sizes is controlled by the competition between particle growth, which may happen via a number of mechanisms, and scavenging of clusters by larger pre-existing particles. Particle growth or activation may (and, in fact, probably does) occur due to the condensation of extra vapours not involved in the initial particle formation process (such as low-volatility organics). Evidence, both theoretical and recently experimental (Kulmala et al., 2007b), is mounting to suggest that large amounts of charged and neutral clusters are almost always present in the atmosphere. Thus the second step of particle activation by extra, condensable vapours is likely to be the limiting step in the production of atmospheric particles. Once activated, continued condensation of vapours is required for particles to grow quickly to sizes greater than ~40 nm where they can participate in the direct and indirect effects of aerosols on climate. See Kulmala and Kerminen (2008) for a thorough discussion of the current state of knowledge regarding the secondary formation and growth of atmospheric particles.

Sulphates dominate the sub-micrometre particle number concentration in the MBL (Fitzgerald, 1991). Sulphuric acid may be derived from the oxidation of di-methyl sulphide (DMS) emitted by marine algae and phytoplankton (Cox and Sandalls, 1974; Lovelock et al., 1972). However, despite a significant number of field measurements, observations of sulphate particle formation in the MBL are rare. Clarke et al. (1998) observed a nucleation event on the Pacific Ocean during a 360 km long near-surface flight and linked the observed new particle formation event after precipitation to naturally produced DMS. However, the measurements combined with dynamic modelling of binary H_2SO_4-H_2O nucleation showed that sulphuric acid concentrations were too low for binary nucleation to occur and a third gas, likely ammonia, was posited to have induced a ternary nucleation process. Pirjola et al (2000) also showed that, under typical conditions in the MBL, binary H_2SO_4-H_2O nucleation will not occur and ternary H_2SO_4-H_2O-NH_4 nucleation will only occur infrequently to produce particles with a detectable size (>3 nm). Within the free troposphere the conditions for DMS induced nucleation are much more probable due to the lower temperature and lower existing particle surface. Nucleation events have been observed in the outflow of clouds during aircraft flights (Clarke and Kapustin, 2002; de Reus et al., 2001; Perry and Hobbs, 1994; Zaizen et al., 1996) as well as due to the entrainment of freshly nucleated particles from the free troposphere during dynamic weather events such as the passage of cold fronts (Bates et al., 1998; Covert et al., 1996).

Coastal nucleation events occurring locally in the boundary layer are much more frequently observed than nucleation events occurring over the remote ocean. Most of our information about coastal nucleation is based on comprehensive measurements performed at one location in particular: Mace Head, Ireland, where nucleation of particles has been observed on almost a daily basis for more than 15 years. These events correlate with tide and solar irradiance. However, dynamic modelling combined with precursor gas concentration measurements, TEM analysis and hygroscopic growth factor measurements have shown that sulphuric acid does not drive the particle production seen at this site (even if it potentially participates in the initial formation of stable atmospheric clusters). Instead, O'Dowd and Hoffman (2005) and references therein, suggested that during low tide the exposed marine biota emits iodine-containing compounds that act as the gas responsible for driving particle growth to detectable sizes. There is also evidence that secondary organic compounds contribute to nucleation mode particle growth at this site at sizes greater than about 5-6 nm (Vaattovaara et al., 2006).

In Moreton Bay on the east coast of Australia, the role of iodine in particle formation and growth is very small or even nonexistent (Johnson et al., 2005). The physicochemical characterisation of 14 and 18nm particles during nucleation events at this site showed that the majority of their volume could be attributed to partially and fully neutralised sulphates (or MSA) plus a volatile organic species. The nucleation mode particles also contained a small fraction (5% by volume) of material that evaporated at ~300-350^{0}C and had iodine-pentoxide-like hygroscopic properties. However, this result is uncertain because at ~300-350^{0}C the diameter of the nucleation mode particles was approaching the lower detection limit of the instrumentation. Consequently, whether particle formation occurred via a sulphate- or iodine-related mechanism in Moreton Bay is still unclear. However, we can conclude that sulphates and/or organics were responsible for particle growth at sizes above 10 nm.

Lee et al. (2008) observed frequent nucleation events in the western coastal region of Korea. Sulphuric acid concentration was higher on event days than non-event days. Similarly at Preila environmental pollution research station on the Curonian Spit in Lithuania, Ulevicius (2002) observed nucleation events on days when the average daily concentrations of SO_2 or NO_2 were two to three times higher than the average monthly concentrations. However, neither of these studies provided enough evidence to completely attribute the events to sulphur-related (as opposed to iodine-related) nucleation. Coastal nucleation events have also been observed at Bodega Bay, California (Wen et al., 2006). During this study, no measurements were performed to identify the precursor responsible for particle nucleation and growth but coastal biogenic activity did play a role. Two studies have observed nucleation events in continentally-affected air masses arriving at coastal measurement sites at Appeldore Island, Maine USA (Russell et al., 2007) and on the north coast of Norfolk, United Kingdom (Coe et al., 2000). In both cases the events were attributed to continental, as opposed to marine/coastal sources. Finally a very recent study has reported particle formation events during low-tide at a coastal site in Brittany, France (Whitehead et al., 2009). Ultra-fine particle emission fluxes were directly linked to both increased ozone depositional loss to exposed macro-algae and the photochemical destruction of ozone. There is the suggestion that this could indicate iodine-mediated new particle formation. Apart from these studies and the large amount of research conducted at Mace Head, few other studies of coastal nucleation events are reported in the literature. The question of whether sulphates or iodine-containing species are responsible for particle formation and growth at other coastal locations around the world is yet to be thoroughly investigated. In the current study we focus only on the question of particle growth at sizes greater than 10 nm.

One method of investigating potential mechanisms of new particle growth is to obtain information about the chemical composition of freshly nucleated particles. Current state-of-the-art techniques cannot measure the composition of stable atmospheric clusters < 3 nm in diameter and, therefore, cannot be used directly to investigate mechanisms of particle formation. Nevertheless a range of techniques exist, which can investigate the composition of particles in the observable nucleation mode size range (3-25 nm) immediately following a nucleation event. These techniques, listed with their approximate ranges of operation are as follows: CPC related physicochemical techniques, range 3-10 nm (Kulmala et al., 2007a; O'Dowd et al., 2002a); Thermal Desorption Chemical Ionisation Mass

Spectrometry (TDCIMS), range 5-20 nm (Smith et al., 2008; Smith et al., 2005; Smith et al., 2004); Aerosol Mass Spectrometry (AMS), lower limit ~20nm (Allan et al., 2006; Zhang et al., 2004); and Tandem Differential Mobility Analysis (TDMA) to measure particle hygroscopicity and/or volatility, lower limit 3nm (e.g. Ehn et al., 2007; Sakurai et al., 2005).

On their own, measurements of particle volatility and/or hygroscopicity place relatively weak constraints on the actual composition of ultra-fine particles because different chemical species can display similar physical properties within a TDMA system. To address this problem the Volatility-Hygroscopicity-Tandem Differential Mobility Analysis (VH-TDMA) technique was developed by Johnson et al. (2004). The VH-TDMA *simultaneously* measures the volatile and hygroscopic properties of atmospheric nanoparticles over a continuous temperature range to produce a unique signature for each particle type. Comparison of VH-TDMA signatures measured in the field with those of laboratory aerosols of known chemical composition can then help determine the composition of the atmospheric particles. Johnson et al. have previously employed this technique in a coastal environment to infer the composition of freshly nucleated particles (Johnson et al., 2005, see above).

In summary, the objective of this study was 1) to identify if, and to what degree new particle formation and growth occurs in a remote, sub-tropical coastal environment and 2) to investigate possible mechanisms of particle growth through indirect determination of the chemical composition of nucleation mode particles using a VH-TDMA system.

Materials and Methods

Site details

Agnes Water is a remote coastal headland located on the East coast of Australia (24.2^0S 151.9^0E) (Fig. 3.1). The exact measurement site was a private dwelling located directly on the beach, far from any local anthropogenic sources of particles such as roads. The site has a large open ocean sector covering the range of bearings from 320-110^0 (all bearings in this paper are measured from true north). Fraser Island (a sand island covered in vegetation) and the tidal flats comprising Hervey Bay (depth<25 m) lay ~150 km away at a bearing of approximately 110-135^0. Further south at a bearing of ~140^0 is the town of Bundaberg. The Great Barrier Reef (GBR) lies to the north of the measurement point. The southernmost reefs of the GBR are approximately 50 km away at a bearing of 050^0. The intensive campaign was conducted over a 4 week period in autumn (March/April) 2007.

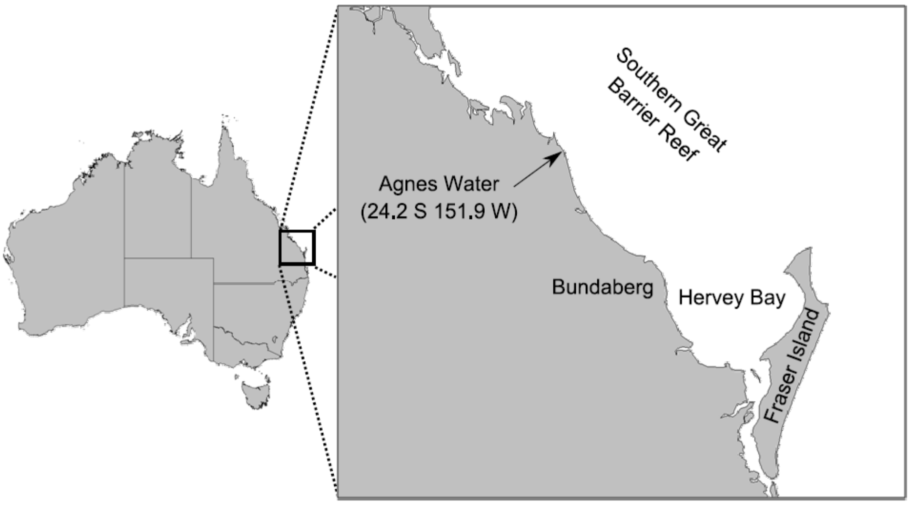


Figure 3.1: Map of Australia detailing the sampling point (Agnes Water) and surroundings.

Instrumentation

Meteorological measurements

A portable weather station (Monitor sensors, Brisbane Australia) was erected directly on the dunes overlooking the beach in front of the house at a sufficient distance from any large objects to prevent local variations in the measured wind speed and direction. The temperature, atmospheric pressure, solar irradiance, wind speed, wind direction and relative humidity were measured at 5 minute intervals throughout the entire campaign. These measurements were validated against 3 hour observations of the same variables collected from a nearby (~2 km) Australian Bureau of Meteorology (BOM) weather station (Town of 1770).

Particle measurements

Size distributions of particles ranging from 4 to 165 nm in diameter were measured using a TSI Scanning Mobility Particle Sizer (consisting of a TSI 3080 short column electrostatic classifier and 3022 CPC operated in low flow mode). The SMPS completed one scan every 5 minutes.

The volatile and hygroscopic properties of particles with diameters from 10 to 110 nm were measured with a VH-TDMA system that is described in detail elsewhere (Fletcher et al., 2007; Johnson et al., 2004). Essentially, the system first electrostatically classifies the sizes of the ambient aerosol to produce a nearly monodisperse distribution of particles around a chosen diameter. These particles are then heated in a low-flow thermodenuder (built in house). After the thermodenuder, the aerosol flow is split; half flows to a dry SMPS (RH<25%) and half flows to a humidified SMPS (see Johnson et al., 2008 for details of the humidification technique). The volatilised-dry particle diameter is taken as the median of the dry size distribution and the volatilised-humidified particle diameter is taken as the median diameter of the humidified size distribution. The output variables of the system recorded at each step of the volatilisation process are volume fraction remaining (V/Vo) - which is obtained from the chosen initial particle diameter and the volatilised-dry diameter - and, diameter Hygroscopic Growth Factor (HGF) which is obtained by dividing the volatilised-humidified diameter by the volatilised-dry diameter. The use of two separate SMPS systems in the VH-TDMA allows the HGF of atmospheric particles to be measured as a function of both humidity (≤95%) and volatilisation temperature (<500^{0}C).

The VH-TDMA technique lends itself particularly well to the analysis of the composition and structure of marine particles because marine aerosols are thought to consist of only a few classes of compounds, each of which has very different volatile and hygroscopic properties. To complement the atmospheric measurements performed for this study we compared them with VH-TDMA measurements of laboratory generated aerosols of known composition that exist in the MBL. In particular, our database of laboratory VH-TMDA data includes measurements of ammoniated sulphates, sulphuric acid, MSA, ammonium nitrate (Johnson et al., 2004), sodium chloride, sea salt, iodine-containing compounds (HIO_3, I_2O_5) (Ristovski et al., 2006) and secondary organic aerosol (photo-oxidation products of α-pinene) (Meyer et al., 2009).

Each presented VH-TDMA scan was performed with a different initial particle size and these are indicated in the individual figures. The initial particle size was chosen slightly above the centre of the nucleation mode (seen by the SMPS) at the beginning of the scan to account for growth of the mode during the scan. The scans involved increasing the thermodenuder temperature from ambient temperature to ~200^0C in 5-10^0C steps. The RH in the humidified SMPS was kept constant at 90% (variation ±0.5% during scan). Volume fraction remaining (V/Vo) and HGF (RH=90%) were simultaneously measured at each volatilisation temperature. Each VH-TMDA scan took ~1-2 hrs to complete.

The SMPS and VH-TDMA were set up on a second floor balcony of the dwelling directly facing the ocean. Ambient aerosol was drawn directly from a ~1m long conductive rubber tube connected to the roof of the balcony through a bipolar Kr85 aerosol neutraliser (TSI model 3077) and into the two instruments. The height of the instruments above the water line was approximately 5m.

Ion size distributions

The appearance of nucleation mode particles was also determined by measurement of the size distributions of atmospheric ions with an Air Ion Spectrometer (AIS, Airel Ltd. Estonia). The AIS measures the mobility distribution of both positive and negative ions spanning a diameter range of approximately 0.34 to 40 nm. The AIS consists of two cylindrical aspiration-type Differential Mobility Analysers (DMA), one for positive and one for negative ions. Each mobility analyser has 21 collector electrodes provided with individual electrometrical amplifiers for measuring the electrical current carried by ions of different mobilities (Mirme et al., 2007). The AIS was located next to the particle instrumentation.

Calculations of the ion and particle growth rates

Particle and ion growth rates (GR) during the nucleation events were calculated from the SMPS and AIS data by tracking the peak nucleation mode diameter over time. SMPS GR’s over particular size ranges are not evaluated as statistically the total number of observed nucleation events is small (because this was a short, intensive campaign) and nucleation mode particles appeared at, grew to and were prominent at different sizes during each event. For this reason the SMPS derived GRs are presented with the corresponding size ranges that the calculations were made over as well as the sample sizes.

Supplementary data

Air mass back trajectories were calculated after the measurement campaign using the GDAS global dataset in the HYSPLIT model (Draxler and Rolph, 2003; Rolph, 2003). For an interesting air mass (e.g. new particle formation event) 96-hour back trajectories were calculated at altitudes of 10, 100, 1000 and 10000m to observe the passage of air in the marine boundary layer (MBL) and free troposphere before the air arrived at Agnes Water.

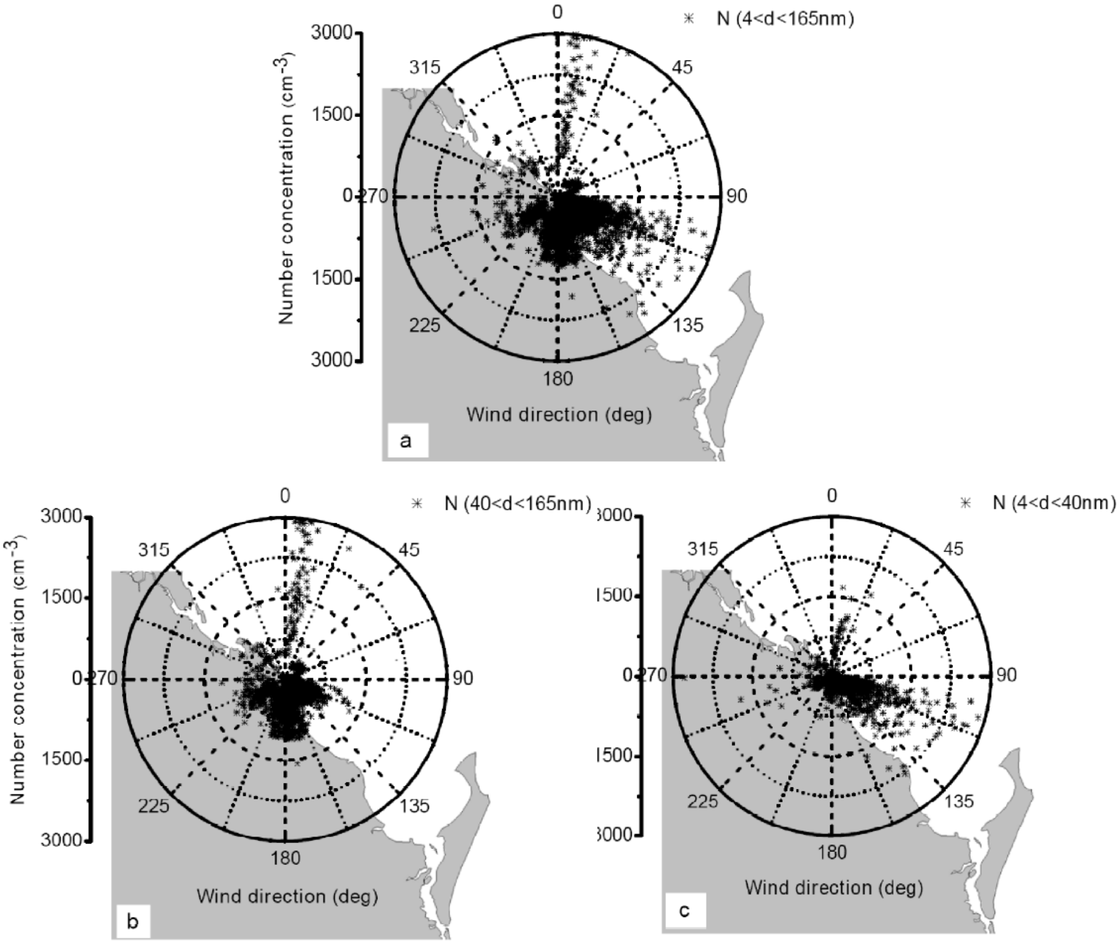


Figure 3.2: Polar plots of number concentration against wind direction for particles in the size range a) 4-165 nm, b) 40-165 nm and c) 4-40 nm.

Results and discussion

Physical characterisation of nucleation events and comparison with meteorological variables

Wind direction

Figure 3.2a is a polar plot of the total concentration of particles measured by the SMPS (4 nm<d<165 nm) as a function of wind direction. It is overlayed onto a map of the area surrounding Agnes Water and centred at the sampling point. The data are gathered into two main groups that reflect the prevailing wind directions during the campaign, which followed a very regular pattern. During the night winds came from the continental sector at bearing of 220-145° while during the day the winds moved progressively east (145-90°) and strengthened as the SE sea breeze commenced by the afternoon. The average concentration of particles ($4<d<165$ nm) over the entire length of the campaign coming from the whole marine/coastal sector (bearing range $320\text{-}135^0$) was 345 cm^{-3}. The corresponding average concentration of particles coming from the continental sector (bearing range $140\text{-}315^0$) was 587 cm^{-3}.

Although there was variation in the wind direction at night and day, the calculated HYSPLIT back trajectories indicate that almost all of the air masses arriving at the sampling point during the night or day had spent at least 96 hours travelling over the open Pacific Ocean S or SE of Australia within the marine boundary layer (MBL) (see Fig. 3.3). The fact that HYSPLIT sees very little difference between the histories of air masses arriving during the night and day could be due to the temporal and/or spatial resolution of the GDAS dataset in the HYPLIT model. However, this fact also presents a possible explanation of why the concentration of particles coming from the continental sector (defined by wind direction) was relatively low (average 587 cm^{-3}); these air masses may have originated over the open ocean and only crossed land briefly before arriving at the sampling point.

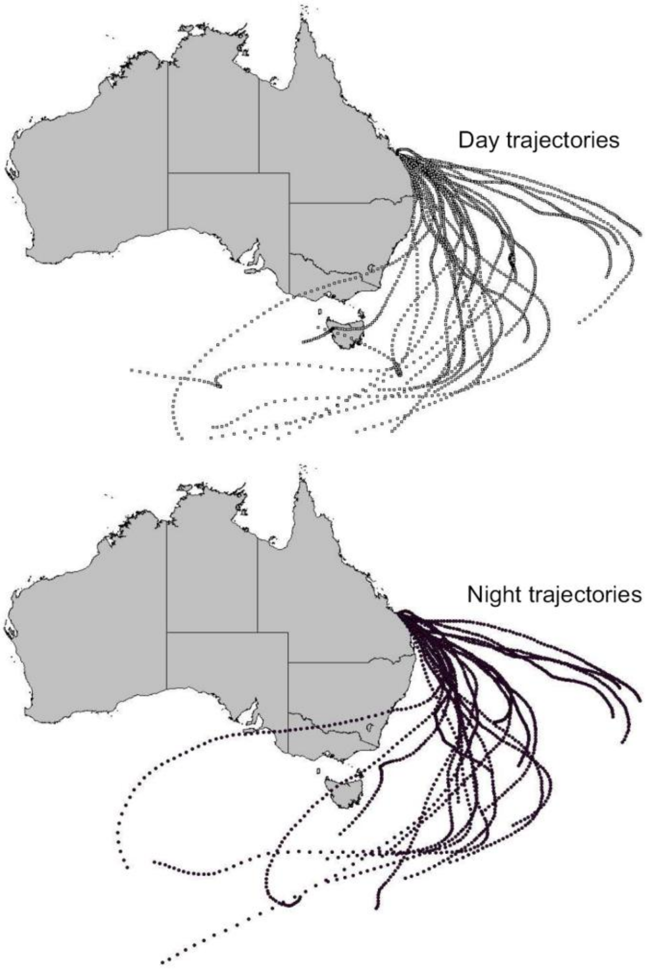


Figure 3.3: HYSPLIT 96-hour back trajectories for air masses arriving at Agnes Water at an altitude of 100 m on each day (12:00 local time) and night (02:00 local time) of the campaign. Note that there was no significant between these trajectories and the trajectories of air masses arriving at altitudes of 10 m and 1000 m.

Nucleation mode particles were observed on 65% of days during the campaign. Back trajectory analysis indicated that the air masses did not arrive from the free troposphere; therefore, the nucleation mode particles must have originated in the MBL. To help identify the MBL source of these particles, two more polar plots are shown in Figures 3.2b and 3.2c. Figure 3.2b shows the concentration of particles with diameter between 40 and 165 nm as a function of wind direction while Fig. 3.2c shows the concentration of particles smaller than 40 nm as a function of wind direction. The dividing diameter of 40 nm between these two figures was chosen because the median diameter of the Aitken mode was very rarely observed below this diameter, while the median diameter of the nucleation mode was frequently observed to grow up to (and sometimes beyond) this diameter. Figure 3.2b indicates that the continental sector produced higher concentrations of Aitken and accumulation mode particles compared to the marine/coastal sector. Over the length of the campaign the average concentration of particles with diameter between 40 and 165 nm coming from the continental sector was 445 cm^{-3}. The corresponding average for particles in this size range coming from the marine/coastal sector was only 196 cm^{-3}. From Figure 3.2c we can see that the occurrence of high concentrations (>1000 cm^{-3}) of particles smaller than 40 nm is significantly more prevalent in the marine sector than in the continental sector.

Ion and particle size distributions

The nucleation mode particles generally disappeared quite abruptly after 1-2 hrs as the wind direction moved more north from 100°. Only 3 days could be classified as having strong nucleation events characterised by a) the clear growth of particles from the nucleation to the Aitken mode and by b) the persistence of such events for longer than 2 hours. Two such strong events occurred on the 27 and 28 March 2007 (Fig. 3.4). Note that according to the classification system described by Buenrostro Mazon et al. (2009) even these very strong nucleation events would be classified as ‘tail events’ rather than ‘events’ because the nucleation mode particles were not observed below 10 nm. The classification scheme of Vana et al. (2008) is more appropriate to apply to this study because it was developed for coastal nucleation events (in particular, at Mace Head) where particle formation happens at a point or line source. According to this scheme all of the nucleation events observed during this campaign would be classified as class III (apple-type) events.

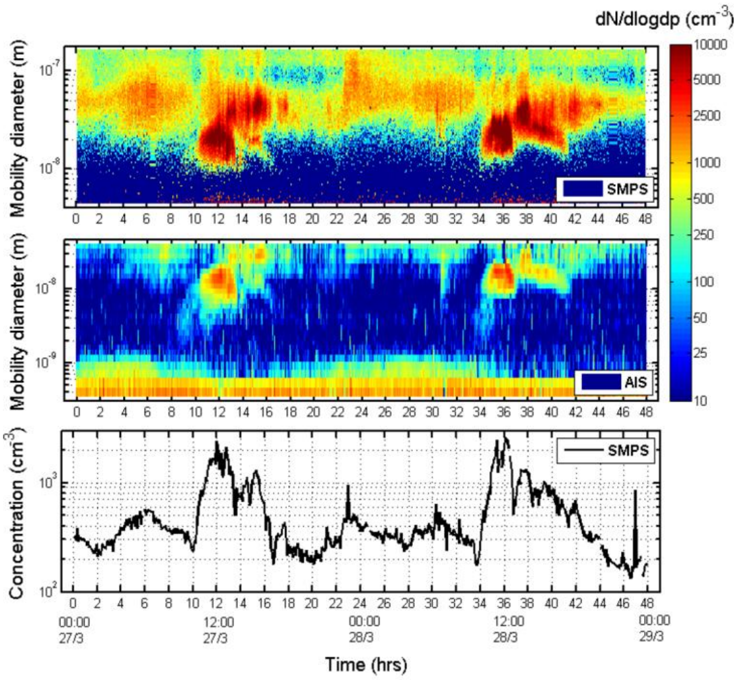


Figure 3.4: Contour plots of the AIS and SMPS data and a time series of particle concentration (4<d<165 nm) for 27 and 28 March 2007. Legends indicate the instrument that measured the data in each graph. AIS data shown is for negative ions, the graph for positive ions looks very similar.

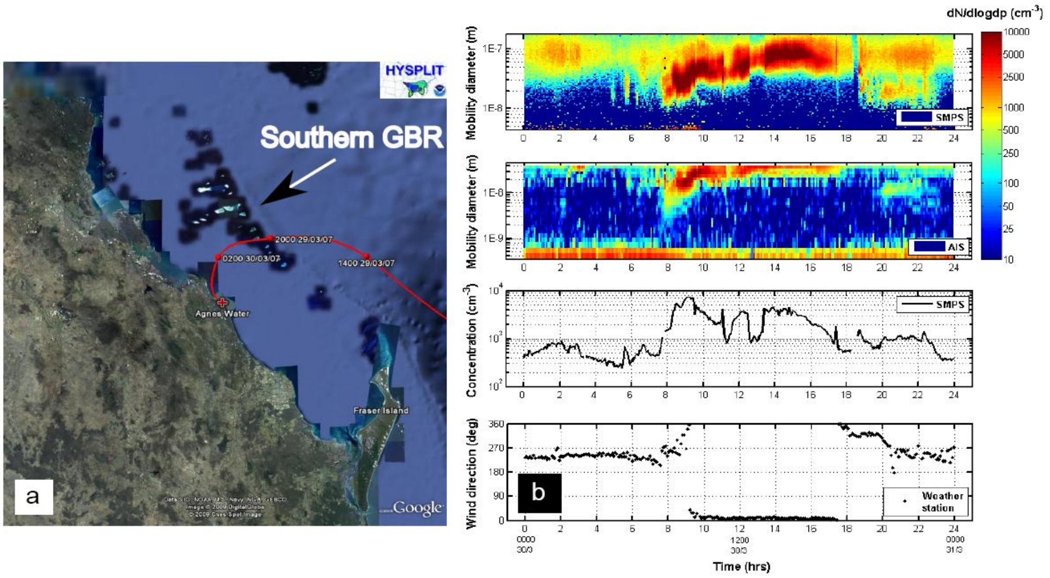


Figure 3.5: a) HYPLIT back trajectory for air mass arriving at Agnes Water at an altitude of 100m at 08:00 on 30 March 2007. The trajectory clearly shows the air mass crossing the southernmost reefs and islands of the Great Barrier Reef (GBR) on the previous night; **b)** Contour plots of the AIS and SMPS data plus time series of particle concentration (4 <d<165 nm) and wind direction for 30 March 2007. Legends indicate the instrument used to measure each data set.

One particular day stands out from the rest. On the day of 30 March 2007 local wind direction was from NNE (10-15^0). This was the only period during the campaign when the local wind blew from this direction. Figures 3.2a, b and c clearly show the elevated concentrations of particles coming from that direction on this particular day. Back trajectories indicated that the air mass had still travelled from the SE, but it had passed Agnes Water before looping in an anti-clockwise direction and travelling back south to the sampling point crossing the southernmost reefs of the GBR on the way (Fig. 3.5a). Based on calculations from both HYSPLIT back trajectories and wind speed data it would have taken 10-20 hrs for the air to travel from the GBR to Agnes Water. Contour plots of the AIS and SMPS data collected on this day (Fig. 3.5b) indicated a very strong nucleation event. Particles (~10 nm) were observed at 08:00 LT. The particles grew very quickly into the Aitken mode (up to ~80 nm) where they persisted for almost the entire day.

Ion and particle growth rates

Interestingly, particle growth was never seen by the AIS to occur from molecular cluster size (<1.5 nm) to the Aitken mode. Nucleation events were always characterised by the abrupt appearance of ~5 nm ions in the AIS data and ~10 nm particles in the SMPS data. We cannot determine whether the discrepancies in initial sizes measured by the AIS and SMPS were due to measurement artifacts or actual physical differences between particles and ions. Nevertheless, particle growth was observed with both instruments during most of the nucleation events. For the majority of nucleation events that occurred in air masses from the marine/coastal sector (100-135°), the SMPS-derived GR varied from 1.8-8.2 nm h^{-1} (Table 3.1). On 30 March 2007, GR for nucleation-mode particles was significantly higher, 15.1 nm h^{-1}.

The AIS-derived GRs for larger ions (7-20 nm) were generally higher than the SMPS derived GRs (Table 3.2). This can be explained by the different size ranges the calculations were performed over. Interestingly, the ion GRs during the nucleation event on 30 March 2007 were similar or smaller than the ion GRs during all other nucleation events, in contrast to the SMPS-derived GR. The GRs

Table 3.1: Nucleation mode particle growth rates (GRs) calculated from the SMPS data

Date in 2007	Growth rate (nm h^{-1})	Size range (nm)	Sample size (no. of data points in regression)
27 March	1.8	17-21	26
28 March	8.2	16-24	15
30 March	15.1	20-46	23
04 April	4	16-20	15
05 April	6.5	17-23	13
06 April	7.2	19-31	18
08 April	2.9	16-22	25
09 April	5.4	15-21	15
10 April	5.8	15-22	18
11 April	7.9	17-25	15
12 April	6.1	12-26	28

Table 3.2: Nucleation mode negative (-) and positive (+) ion growth rates (GRs) calculated from the AIS data. Blank spaces indicate values that could not be reliably measured.

Date in 2007	Growth rate (nm h^{-1})					
	1.5-3 nm		3-7 nm		7-20 nm	
	-	+	-	+	-	+
27 March		0.9		1.9		
28 March			11.2	7.1		
30 March	2.8		8.7	5.8	15.1	12.4
04 April					15.1	5.8
05 April				0.6		14.5
06 April					17	19
08 April	0.4		2.1	2.6	22.5	36.5
09 April	2.7		3.8	5.4	43.3	26.1
10 April	6	1.7	3.5	2.5	19.7	18.6
11 April			3.4	1.8		
12 April					3.6	17.7
14 April						21.4

of both positive and negative smaller ions (1.5-7 nm) are much smaller than the GRs for larger ions. A review by Kulmala et al. (2004) indicated that particle GRs in a range of different environments typically vary between 1-20 nm h^{-1}, although particle GRs as high as 180 nm h^{-1} have been observed close to the coastal source region at Mace Head (Dal Maso et al., 2002; O'Dowd et al., 2007). The GRs observed in this study are slightly higher than particle GRs typically seen in the atmosphere but lower than the GRs observed close to the coast at Mace Head.

Tide height, solar intensity, wind speed and RH

To investigate the necessary conditions for new particle formation, we compared time series of particle concentration, tide height (Agnes Water), solar intensity, wind speed, wind direction and RH during strong and weak nucleation events (Figs. 3.6 and 3.7, respectively). The strong nucleation events plotted in Fig. 3.6 are the same events plotted in Fig. 3.4 and the weak events occurred daily from 6 to 9 April 2007. The oscillation in the wind direction from the continental to marine/coastal sector from night to day (and corresponding increase in wind speed) is seen in both Figs. 3.6 and 3.7. Immediately before each event there was a decrease in particle concentration corresponding to the daily shift in the wind direction from the continental to the marine/coastal sector. The observed nucleation events caused total particle concentration to increase from several hundred particles/cm^3, typical for remote marine background concentrations, to over 1000 particles/cm^3 during the nucelation events. The majority of nucleation events occurred at ~10:00 LT although some events appeared later in the day at 12:00-13:00. This means solar intensity was very high (~1000 W m^{-2}) during each nucleation event and RH was relatively low (~50-60%). A striking feature of the nucleation events is that they are not related to tide height at the measurement site.

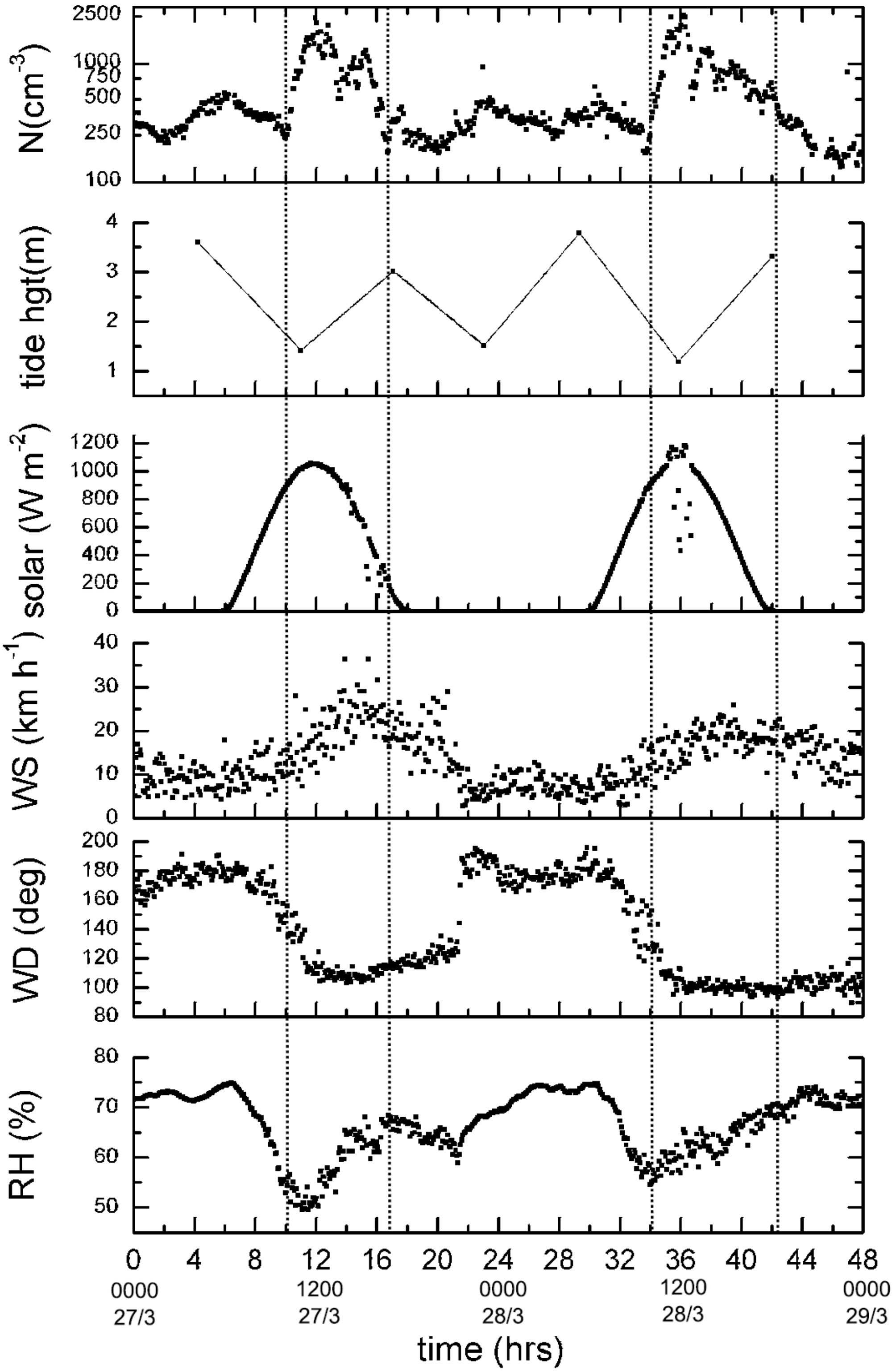


Figure 3.6: Time series of particle concentration (4<d<165 nm), N (cm^{-3}); tide height at Agnes Water, tide hgt (m); solar intensity, solar (W m^{-2}); wind speed, WS (km h^{-1}); wind direction from true north, WD (deg); and relative humidity, RH (%) for 27 and 28 March 2007. Dashed lines indicate the occurrence of 2 strong nucleation events.

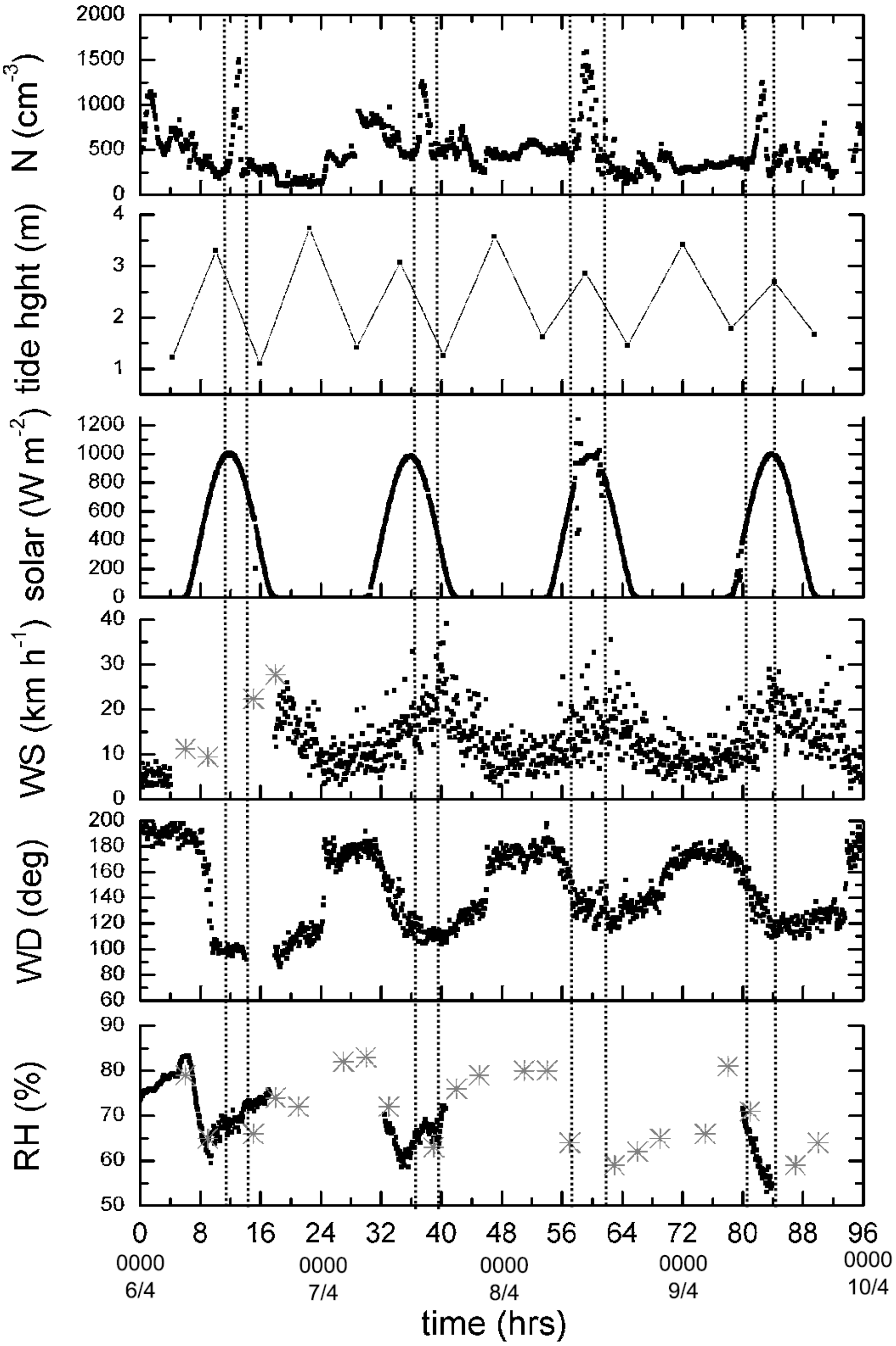


Figure 3.7: Time series of particle concentration (4<d<165 nm), N (cm^{-3}); tide height at Agnes Water, tide hgt (m); solar intensity, solar (W m^{-2}); wind speed, WS (km h^{-1}); wind direction from true north, WD (deg); and relative humidity, RH (%) for 06 to 09 April 2007. Dashed lines indicate the occurrence of 4 weak nucleation events. Grey asterisks represent data collected from a nearby (Town of 1770) Australian Bureau of Meteorology weather station.

To further examine the relationship between event occurrence and tide height we calculated the number distribution of nucleation events as a function of the time in hours between the beginning of a nucleation event and low tide (Δt). Negative Δt values indicate that low tide occurred after the nucleation event began (that is, the event occurred after a high tide). This was first done for tide data from Agnes Water (measurement location). The majority of air masses in which nucleation events occurred also passed over another coastal area surrounding Fraser Island some 150 km upwind of the measurement site. The times when the air masses containing nucleation mode particles (observed at Agnes Water) passed over this coastal region were back-calculated according to measured wind speed data at Agnes Water and Fraser Island, and these were used to calculate the number Δt distribution for this area. The tide data in this case was taken not from Agnes Water but from Fraser Island. Both distributions are relatively flat and uniform considering the data has been grouped into coarse, 2 hour time bins (Fig. 3.8). If there was a relationship between nucleation event and tide height we would expect to see a spike in the distributions in one of the Δt time bins. Rather, it was at least as likely for a nucleation event to occur after a high tide than a low tide. Therefore we conclude that there is no relationship between event occurrence and tide height. This finding is not particularly surprising for the Agnes Water measurement site because tidal amplitude was relatively small (average 0.9 m) and no visually obvious marine biota was exposed at low tides along the beach.

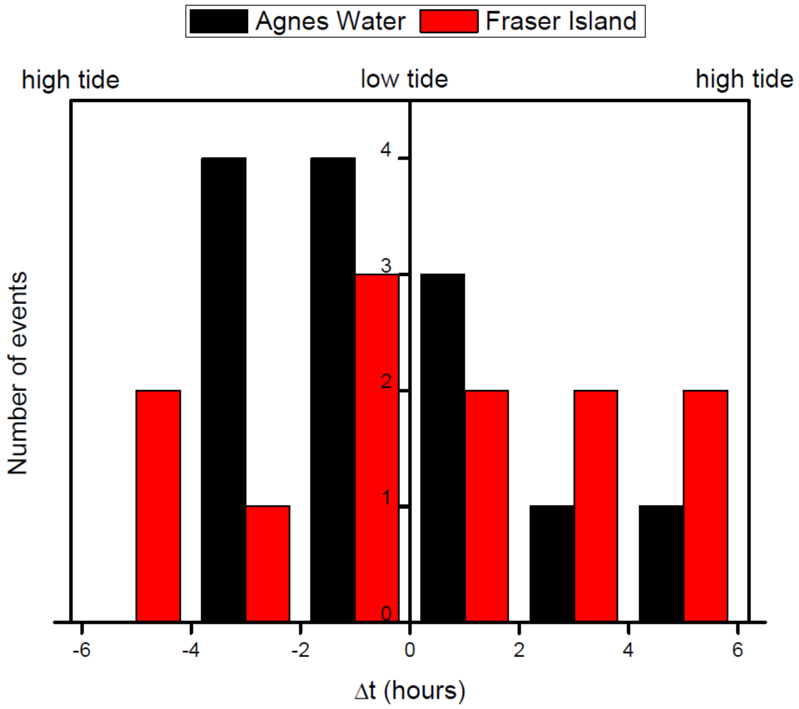


Figure 3.8: The number distribution of nucleation events as a function of the time between the beginning of a nucleation event and low tide (Δt). Data is grouped into 2 hour time bins. Distributions are shown for two coastal regions; Agnes Water and Fraser Island (see text for details). The average time between low and high tides during the campaign was 6.2 hrs.

Physicochemical characterisation of nucleation mode particles

Figure 3.9 presents typical VH-TDMA scans on nucleation mode particles during one strong and one weak nucleation event. Each VH-TDMA scan showed a two-step volatilisation process and corresponding change in HGF which means the nucleation mode particles contained two components of differing volatility and hygroscopicity. Because the two components have different HGFs, there would be two modes in the humidified size distributions if the components were externally mixed. Only one mode was ever observed in the humidified size distributions, which indicates that these two components were internally mixed within the nucleation mode particles. For particles observed during the strong nucleation event (top of Fig. 3.9) the transition between the two components was very pronounced. The first component was relatively volatile and completely evaporated by ~110^0C where the volatility curve flattened out. Over the same temperature range HGF increased rather abruptly from 1.26 to 1.44. For particles observed during the weak nucleation event (bottom of Fig. 3.9) the volatilisation of the first component was more gradual as temperature increased. This was also reflected by the gradual increase in HGF with temperature. Whether gradual or abrupt, the increase in HGF as the first component evaporated means that this component was less hygroscopic than the second component. This information and the fact that the first component was relatively volatile (more so than sulphates) indicate that this component was most likely organic.

The volatilisation temperature of the second component corresponded to the volatilisation temperature of ammoniated sulphate (partially or fully neutralised sulphuric acid) nanoparticles. To further investigate this in Fig. 3.9 we compared ambient data with the volatility curves for 29 nm ammonium sulphate (AS) particles generated by atomising a dilute solution of ammonium sulphate in ultra-pure de-ionised water. Excellent agreement was obtained between the ambient and laboratory measurements when the volatility curves of the laboratory generated AS particles were normalised to the apparent volume fraction of the second component in each VH-TDMA scan. The measured HGFs of the nucleation mode particles also approached the modelled, dry size dependent AS HGF curves (Fig. 3.9). Therefore, based on the combined volatility and hygroscopic data, we can conclude that the second component of the nucleation mode aerosol was most probably ammoniated sulphate. Unfortunately, our method is unable to determine the degree of neutralisation of the ammoniated sulphate particles as partially and fully neutralised sulphate particles have similar growth factors and decompose via the same route. However, our results still clearly show that the majority of the volume of these nucleation mode particles can be attributed to internally mixed sulphate and organic components. Assuming that the particles were only composed of these two species, the 17 nm particles observed during the strong nucleation event consisted of ~60% sulphates-40% organics by volume and the 22.5 nm particles observed during the weak nucleation event consisted of ~76% sulphates- 24% organics by volume.

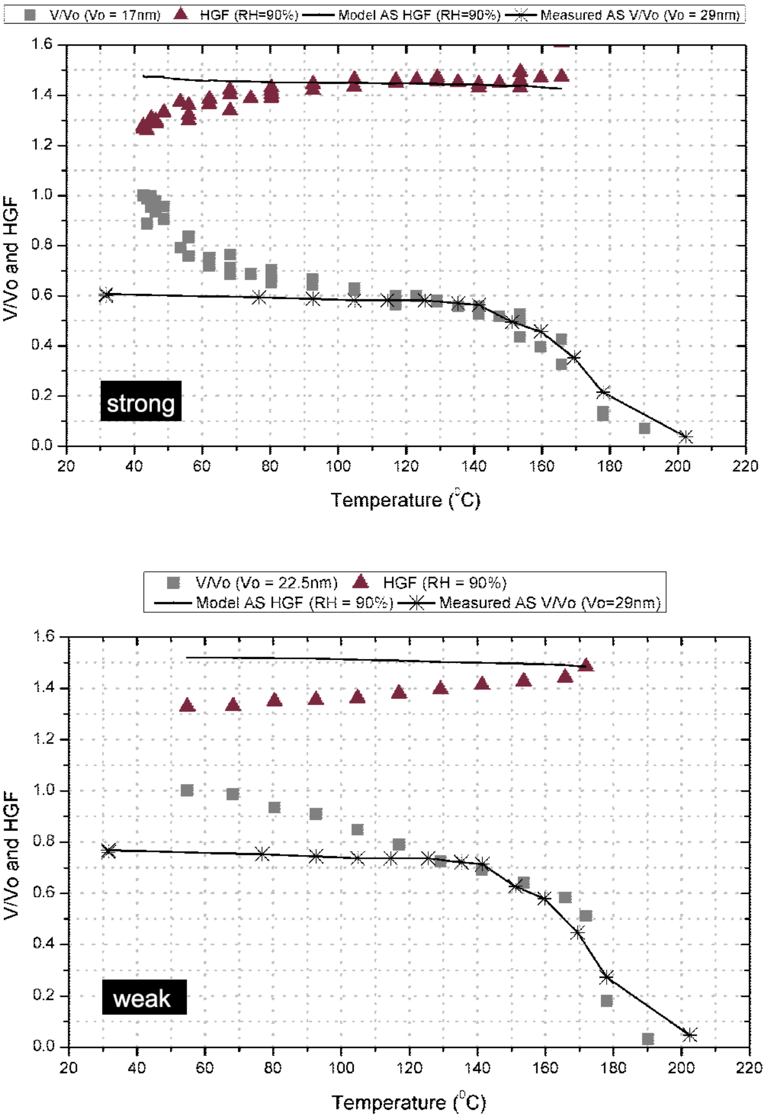


Figure 3.9: VHTDMA scans completed during a strong (top) and weak (bottom) nucleation event. V/Vo is volume fraction remaining and HGF (RH=90%) is the growth factor at 90% RH for the atmospheric particles. The solid black lines indicate measured volatility curve of ammonium sulphate (AS) particles normalised to the apparent volume fraction of the more hygroscopic component and theoretical, dry size dependent ammonium sulphate growth factors.

Comparison with other coastal nucleation sites

Besides Mace Head there are only few locations where coastal nucleation events have been observed but unfortunately without detailed analysis of particle formation and growth mechanisms and particle precursor sources. Therefore we will focus on comparing our results with the results from Mace Head.

The nucleation events observed during this study were characterised by the appearance of a nucleation mode with peak diameter >10 nm. At Mace Head the size at which the nucleation mode occurred depended on the distance of the tidal source region and varied from 3 to 10nm for source region distances from 100m to more than 10km, respectively (O'Dowd et al., 2002c). In our case the particles grew at a rate from 1.8-8.2 nm h^{-1}, which is significantly lower than the growth rate of nucleation mode particles observed at Mace Head (Dal Maso et al., 2002; O'Dowd et al., 2007). The initial appearance of larger particles with lower growth rates in this study indicates that the source region for nucleation mode aerosol is further away from the measurement point. Assuming constant GRs we calculated that the source region is at a distance greater than 20 km from the measurement site. It is worth mentioning that in other locations such as forests the observed growth rates even close to the source are much lower indicating that the source location could be even further away.

Similarly to the events observed at Mace Head, solar radiation was a necessary condition for a nucleation event to occur, indicating that photochemical oxidation processes were an important stage in new particle formation. In contrast to the Mace Head observations, the occurrence of a nucleation event was not related to tide height during this study. Although a relationship between particle production and low tide has been observed at Mace Head and other coastal sites (Bigg and Turvey, 1978; Johnson et al., 2005; O'Dowd et al., 2002b; Whitehead et al., 2009), coastal particle production that is not related to tide height has been observed before at Bodega Bay, California (Wen et al., 2006).

Finally, iodine-containing compounds released by exposed macro-algae are primarily responsible for the particle production observed at Mace Head (O'Dowd and Hoffmann, 2005). Physicochemical characterisation of nucleation mode particles (17-22.5 nm) during both strong and weak nucleation events in clean, marine air masses at Agnes Water indicated that the majority of their volume could be attributed to sulphate and organic components. It should be reiterated that the lower size limit of our VH-TMDA was 10 nm. Therefore from this analysis we cannot make any conclusions regarding the species that participated in the initial particle formation and growth processes. However, we can make conclusions regarding the mechanism responsible for particle growth at sizes greater than 10 nm. Simple calculations using basic polydisperse coagulation theory (Baron and Willeke, 2001) show that for the observed nucleation mode concentrations the process of coagulation could only account for a very small fraction of the observed particle growth rates (1.8-8.2 nm h^{-1}). This means the majority of nucleation mode particle growth most likely occurred due to the condensation of sulphates and/or organic vapours. No evidence was obtained in this study to suggest that iodine-containing compounds were involved in new particle growth. Nevertheless we can not rule out the possibility that such compounds participated in the initial stages of particle formation and growth.

Possible particle precursor sources

The question remains: what was the source of the particle precursors and the sulphur/organic vapours that were responsible for observed particle growth at Agnes Water? Nucleation events generally occurred when wind direction was from the marine/coastal sector covering the range of bearings 100–145° (see Fig. 3.2c). This sector contains the shallow, biologically-active waters of Hervey Bay, the vegetation covered Fraser Island and the open ocean. This does not necessarily indicate that these marine/coastal regions contained the sources responsible for particle formation and growth because the land-sea breeze effect must be taken into account. This effect refers to the oscillation in local wind direction from the continent (160–200°) during the night to the ocean/coast (100–145°) during the day. It is clearly seen in the periodic nature of the wind direction time series (Figs. 3.6 and 3.7) but not in the HYSPLIT back trajectories (Fig. 3.3). Particle precursors may have been emitted from the continent and advected offshore during the night, before being photo-oxidised, nucleated into the particle phase and carried back to our coastal measurement site as solar intensity increased and the wind direction moved progressively east during the morning. The fact that nucleation event occurrence did not depend on tidal height (Fig. 3.8) supports this hypothesis.

However, there is also evidence to suggest that the precursor vapours were actually of marine/coastal origin. Firstly, the change in wind direction from the continental to the marine/coastal sector was almost always accompanied by a decrease in particle number concentration. This indicates that the continentally affected air masses were being diluted by cleaner, marine air as the local wind direction changed from land to sea. If the vapours responsible for particle formation and growth were of continental origin, they would have been progressively more diluted as the sea breeze moved further east and strengthened throughout the day. Despite this nucleation events were still observed up to 3 hrs after the land-sea shift in wind direction (e.g. 6 and 7 April 2007; Fig. 3.7). In addition during the strong nucleation events particle growth is observed throughout the whole day (e.g. Figs. 3.4 and 3.5), which indicates a fairly constant vapour source. Therefore on the balance of the evidence we believe that the vapours responsible for particle formation and growth were most likely of marine/coastal origin. In particular, the biologically-rich waters of Hervey Bay and coastal region of Fraser Island are likely source regions for particle precursors. Nevertheless without any measurements of anthropogenic or continental tracers (e.g. black carbon, carbon monoxide, radon) we cannot prove this hypothesis by ruling out continental precursor sources.

The above discussion does not apply to the large nucleation event observed on 30 March 2007. No air masses with the same history, excepting the passage over the GBR, had such strong nucleation events throughout the campaign. Particle GR was also much higher during this event compared to all other events during the campaign (although ion GR was not). This suggests that the precursor source of these particles was different, or stronger, than the precursor source for all other nucleation events. The initial size of the nucleation mode particles observed at Agnes Water was ~10 nm, which indicates particle formation occurred somewhere upwind of the sampling point. Therefore we suggest that the GBR was the likely source of precursor vapours for these freshly formed particles. Coral reefs comprising the GBR are known to be large sources of DMS (Broadbent and Jones, 2004) and the GBR has long been suspected as a major source of freshly nucleated particles (Bigg and Turvey, 1978). However to our knowledge this is the first direct observation of particle formation from the GBR. Unfortunately on this day no physicochemical characterisation of the nucleation mode particles was completed and the mechanism of particle growth remains unknown. The particles produced from the GBR grew quickly up to ~80 nm in diameter. If we assume that similar particle production occurs along the whole 2600 km length of the GBR then it would constitute a major, natural source of ultrafine particles and cloud condensation nuclei (CCN) that would have a very significant role in regulating climate.

Conclusions

Coastal nucleation events were observed on 65% of the days during a month-long measurement campaign at the remote coastal location of Agnes Water. The events occurred in clean, marine air masses that had travelled from the SE over Hervey Bay. Solar intensity was high (~1000 W m^{-2}) and RH was low (~60%) during each event but there was no relationship between event occurrence and tide height. The growth rates of the nucleated particles were relatively high (1.8-8.2 nm h^{-1}). Nucleation mode concentrations were too low for coagulation to have a significant contribution to these observed growth rates. Therefore the condensation of low-volatility vapours was responsible for the majority of new particle growth. Based on the physicochemical characterisation of 17-22.5 nm particles with a VH-TDMA during both strong and weak nucleation events, we attributed the majority of the volume of nucleated particles to sulphate and organic components. Therefore we conclude that the condensation of sulphate and/or organic vapours was most likely responsible for the growth of freshly nucleated particles to climatically relevant sizes. It is possible that particle precursor vapours had a continental or a marine/coastal origin. However, based on all the available data, we suggest that the precursors were most likely coming from marine/coastal sources. In addition, a unique and particularly strong nucleation event observed under northerly winds was attributed to the Great Barrier Reef.

Acknowledgements

This work was funded by the International Laboratory for Air Quality and Health. The authors gratefully acknowledge the NOAA Air Resources Laboratory for provision of the HYSPLIT model (http://www.ready.noaa.gov).

References

Allan, J. D., Alfarra, M. R., Bower, K. N., Coe, H., Jayne, J. T., Worsnop, D. R., Aalto, P. P., Kulmala, M., Hyötyläinen, T., Cavalli, F., and Laaksonen, A.: Size and composition measurements of background aerosol and new particle growth in a Finnish forest during QUEST 2 using an Aerodyne Aerosol Mass Spectrometer, Atmos. Chem. Phys., 6, 315-327, 2006.

Baron, P. A., and Willeke, K.: Aerosol Measurement - Principles, Techniques, and Applications (2nd Edition), John Wiley & Sons, New York, 2001.

Bates, T. S., Kapustin, V. N., Quinn, P. K., Covert, D. S., Coffman, D. J., Mari, C., Durkee, P. A., De Bruyn, W. J., and Saltzman, E. S.: Processes controlling the distribution of aerosol particles in the lower marine boundary layer during the First Aerosol Characterization Experiment (ACE 1), J. Geophys. Res., 103, 16,369–316,383, 1998.

Bigg, E. K., and Turvey, D. E.: Sources of atmospheric particles over Australia, Atmos. Env., 12, 1643-1655, 1978.

Broadbent, A. D., and Jones, G. B.: DMS and DMSP in mucus ropes, coral mucus, surface films and sediment pore waters from coral reefs in the Great Barrier Reef, Mar. Freshw. Res., 55, 849-855, 2004.

Buenrostro Mazon, S., Riipinen, I., Schultz, D. M., Valtanen, M., Dal Maso, M., Sogacheva, L., Junninen, H., Nieminen, T., Kerminen, V.-M., and Kulmala, M.: Classifying previously undefined days from eleven years of aerosol-particle-size distribution data from the SMEAR II station, Hyytiälä, Finland, Atmos. Chem. Phys., 9, 667-676, 2009.

Clarke, A. D., Davis, D., Kapustin, V. N., Eisele, F., Chen, G., Paluch, I., Lenschow, D., Bandy, A. R., Thornton, D., Moore, K., Mauldin, L., Tanner, D., Litchy, M., Carroll, M. A., Collins, J., and Albercook, G.: Particle Nucleation in the Tropical Boundary Layer and Its Coupling to Marine Sulfur Sources, Science, 282, 89-92, 10.1126/science.282.5386.89, 1998.

Clarke, A. D., and Kapustin, V. N.: A Pacific Aerosol Survey. Part I: A Decade of Data on Particle Production, Transport, Evolution, and Mixing in the Troposphere, J. Atmos. Sci., 59, 363-382, 2002.

Coe, H., Williams, P. I., McFiggans, G., Gallagher, M. W., Beswick, K. M., Bower, K. N., and Choularton, T. W.: Behavior of ultrafine particles in continental and marine air masses at a rural site in the United Kingdom, J. Geophys. Res., 105, 26,891–826,905, 2000.

Covert, D. S., Kapustin, V. N., Bates, T. S., and Quinn, P. K.: Physical properties of marine boundary layer aerosol particles of the mid-Pacific in relation to sources and meteorological transport, J. Geophys. Res., 101, 6919–6930, 1996.

Cox, R. A., and Sandalls, F. J.: The photo-oxidation of hydrogen sulphide and dimethyl sulphide in air, Atmos. Env., 8, 1269-1281, 1974.

Dal Maso, M., Kulmala, M., Lehtinen, K. E. J., Mäkelä, J. M., Aalto, P., and O'Dowd, C. D.: Condensation and coagulation sinks and formation of nucleation mode particles in coastal and boreal forest boundary layers, J. Geophys. Res., 107, doi:10.1029/2001JD001053, 2002.

de Reus, M., Krejci, R., Williams, J., Fischer, H., Scheele, R., and Ström, J.: Vertical and horizontal distributions of the aerosol number concentration and size distribution over the northern Indian Ocean, J. Geophys. Res., 106, 28,629–628,641, 2001.

Draxler, R. R., and Rolph, G. D.: HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html) NOAA Air Resources Laboratory, Silver Spring, MD., 2003.

Ehn, M., Petäjä, T., Aufmhoff, H., Aalto, P., Hämeri, K., Arnold, F., Laaksonen, A., and Kulmala, M.: Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid, Atmos. Chem. Phys., 7, 211-222, 2007.

Fitzgerald, J. W.: Marine aerosols: A review, Atmos. Env., 25, 533-545, 1991.

Fletcher, C. A., Johnson, G. R., Ristovski, Z. D., and Harvey, M.: Hygroscopic and volatile properties of marine aerosol observed at Cape Grim during the P2P campaign, Environmental Chemistry, 4, 162-171, 2007.

Johnson, G. R., Ristovski, Z., and Morawska, L.: Method for measuring the hygroscopic behaviour of lower volatility fractions in an internally mixed aerosol, Journal of Aerosol Science, 35, 443-455, 2004.

Johnson, G. R., Ristovski, Z. D., D'Anna, B., and Morawska, L.: Hygroscopic behaviour of partially volatilised coastal marine aerosols using the volatilisation and humidification tandem differential mobility analyser technique, J. Geophys. Res., 110, D20203, doi:10.1029/2004JD005657, 2005.

Johnson, G. R., Fletcher, C., Meyer, N., Modini, R., and Ristovski, Z. D.: A robust, portable H-TDMA for field use, J. Aer. Sci., 39, 850-861, 2008.

Kulmala, M., Pirjola, L., and Makela, J. M.: Stable sulphate clusters as a source of new atmospheric particles, Nature, 404, 66-69, 2000.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aer. Sci., 35, 143-176, 2004.

Kulmala, M., Mordas, G., Petäjä, T., Grönholm, T., Aalto, P. P., Vehkamäki, H., Hienola, A. I., Herrmann, E., Sipilä, M., Riipinen, I., Manninen, H. E., Hämeri, K., Stratmann, F., Bilde, M., Winkler, P. M., Birmili, W., and Wagner, P. E.: The condensation particle counter battery (CPCB): A new tool to investigate the activation properties of nanoparticles, J. Aer. Sci., 38, 289-304, 2007a.

Kulmala, M., Riipinen, I., Sipila, M., Manninen, H. E., Petaja, T., Junninen, H., Maso, M. D., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., and Kerminen, V.-M.: Toward Direct Measurement of Atmospheric Nucleation, Science, 318, 89-92, 10.1126/science.1144124, 2007b.

Kulmala, M., and Kerminen, V.-M.: On the formation and growth of atmospheric nanoparticles, Atmos. Res., 90, 132-150, 2008.

Lee, Y.-G., Lee, H.-W., Kim, M.-S., Choi, C. Y., and Kim, J.: Characteristics of particle formation events in the coastal region of Korea in 2005, Atmos. Env., 42, 3729-3739, 2008.

Lovelock, J. E., Maggs, R. J., and Rasmussen, R. A.: Atmospheric Dimethyl Sulphide and the Natural Sulphur Cycle, Nature, 237, 452-453, 1972.

Meyer, N. K., Duplissy, J., Gysel, M., Metzger, A., Dommen, J., Weingartner, E., Alfarra, M. R., Prevot, A. S. H., Fletcher, C., Good, N., McFiggans, G., Jonsson, Å. M., Hallquist, M., Baltensperger, U., and Ristovski, Z. D.: Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and un-seeded SOA particles, Atmos. Chem. Phys., 9, 721-732, 2009.

Mirme, A., Tamm, E., Mordas, G., Vana, M., Uin, J., Mirme, S., Bernotas, T., Laakso, L., Hirsikko, A., and Kulmala, M.: A wide-range multi-channel Air Ion Spectrometer, Boreal Env. Res., 12, 247-264, 2007.

O'Dowd, C. D., Aalto, P., Hmeri, K., Kulmala, M., and Hoffmann, T.: Aerosol formation: Atmospheric particles from organic vapours, Nature, 416, 497-498, 2002a.

O'Dowd, C. D., Hämeri, K., Mäkelä, J. M., Pirjola, L., Kulmala, M., Jennings, S. G., Berresheim, H., Hansson, H.-C., de Leeuw, G., Kunz, G. J., Allen, A. G., Hewitt, C. N., Jackson, A., Viisanen, Y., and Hoffmann, T.: A dedicated study of New Particle Formation and Fate in the Coastal Environment (PARFORCE): Overview of objectives and achievements, J. Geophys. Res., 107, doi:10.1029/2001JD000555, 2002b.

O'Dowd, C. D., Hämeri, K., Mäkelä, J. M., Väkeva, M., Aalto, P., de Leeuw, G., Kunz, G. J., Becker, E., Hansson, H.-C., Allen, A. G., Harrison, R. M., Berresheim, H., Kleefeld, C., Geever, M., Jennings, S. G., and Kulmala, M.: Coastal new particle formation: Environmental conditions and aerosol physicochemical characteristics during nucleation bursts, J. Geophys. Res., 107, doi:10.1029/2000JD000206, 2002c.

O'Dowd, C. D., and Hoffmann, T.: Coastal New Particle Formation: A Review of the Current State-Of-The-Art, Environ. Chem., 2, 245-255, 2005.

O'Dowd, C. D., and De Leeuw, G.: Marine aerosol production: A review of the current knowledge, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 365, 1753-1774, 2007.

O'Dowd, C. D., Yoon, Y. J., Junkerman, W., Aalto, P., Kulmala, M., Lihavainen, H., and Viisanen, Y.: Airborne measurements of nucleation mode particles I: coastal nucleation and growth rates, Atmos. Chem. Phys., 7, 1491-1501, 2007.

Perry, K. D., and Hobbs, P. V.: Further evidence for particle nucleation in clear air adjacent to marine cumulus clouds, J. Geophys. Res., 99, 22,803–822,818, 1994.

Pijola, L., O'Dowd, C. D., Brooks, I. M., and Kulmala, M.: Can new particle formation occur in the clean marine boundary layer?, J. Geophys. Res., 105, 26531-26546, 2000.

Ristovski, Z. D., Fletcher, C., D’Anna, B., Johnson, G. R., and Bostrom, J. T.: Characterization of iodine particles with Volatilization-Humidification Tandem Differential Mobility Analyser (VH-TDMA), Raman and SEM techniques, Atmos. Chem. Phys. Discuss., 6, 1481-1508, 2006.

Rolph, G. D.: Real-time Environmental Applications and Display System (READY), Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD., 2003.

Russell, L. M., Mensah, A. A., Fischer, E. V., Sive, B. C., Varner, R. K., Keene, W. C., Stutz, J., and Pszenny, A. A. P.: Nanoparticle growth following photochemical a- and b-pinene oxidation at Appledore Island during International Consortium for Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals 2004, J. Geophys. Res., 112, D10S21, doi:10.1029/2006JD007736, 2007.

Sakurai, H., Fink, M. A., McMurry, P. H., Mauldin, L., Moore, K. F., Smith, J. N., and Eisele, F. L.: Hygroscopicity and volatility of 4-10 nm particles during summertime atmospheric nucleation events in urban Atlanta, J. Geophys. Res., 110, D22S04, doi:10.1029/2005JD005918, 2005.

Smith, J. N., Moore, K. F., McMurry, P. H., and Eisele, F. L.: Atmospheric Measurements of Sub-20 nm Diameter Particle Chemical Composition by Thermal Desorption Chemical Ionization Mass Spectrometry, Aer. Sci. Tech., 38, 100-110, 2004.

Smith, J. N., Moore, K. F., Eisele, F. L., Voisin, D., Ghimire, A. K., Sakurai, H., and McMurry, P. H.: Chemical composition of atmospheric nanoparticles during nucleation events in Atlanta, J. Geophys. Res., 110, D22S03, doi:10.1029/2005JD005912, 2005.

Smith, J. N., Dunn, M. J., VanReken, T. M., Iida, K., Stolzenburg, M. R., McMurry, P. H., and Huey, L. G.: Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth, Geophys. Res. Lett., 35, L04808, doi:10.1029/2007GL032523, 2008.

Ulevicius, V., Mordas, G., and Plauskaite, K.: Evolution of aerosol particle size distribution in the coastal environment: effect of relative humidity, SO_2 and NO_2, Environ. Chem. Phys., 24, 13-17, 2002.

Vaattovaara, P., Huttunen, P. E., Yoon, Y. J., Joutsensaari, J., Lehtinen, K. E. J., O'Dowd, C. D., and Laaksonen, A.: The composition of nucleation and Aitken modes particles during coastal nucleation events: evidence for marine secondary organic contribution, Atmos. Chem. Phys., 6, 4601-4616, 2006.

Vana, M., Ehn, M., Petäjä, T., Vuollekoski, H., Aalto, P., De Leeuw, G., Ceburnis, D., O'Dowd, C. D., and Kulmala, M.: Characteristic features of air ions at Mace Head on the west coast of Ireland, Atmos. Res., 90, 278-286, 2008.

Wen, J., Zhao, Y., and Wexler, A. S.: Marine particle nucleation: Observation at Bodega Bay, California, J. Geophys. Res., 111, doi:10.1029/2005JD006210, 2006.

Whitehead, J. D., McFiggans, G. B., Gallagher, M. W., and Flynn, M. J.: Direct linkage between tidally driven coastal ozone deposition fluxes, particle emission fluxes, and subsequent CCN formation, Geophys. Res. Lett., 36, doi:10.1029/2008GL035969, 2009.

Zaizen, Y., Ikegami, M., Tsutsumi, Y., Makino, Y., Okada, K., Jensen, J., and Gras, J. L.: Number concentration and size distribution of aerosol particles in the middle troposphere over the Western Pacific Ocean, Atmos. Env., 30, 1755-1762, 1996.

Zhang, Q., Stanier, C. O., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Pandis, S. N., and Jimenez, J. L.: Insights into the Chemistry of New Particle Formation and Growth Events in Pittsburgh Based on Aerosol Mass Spectrometry, Env. Sci. Tech., 38, 4797-4809, doi:10.1021/es035417u, 2004.

Chapter 4: Observation of the suppression of water uptake by marine particles

R. L. Modini[1], G. R. Johnson[1], C. He[1], Z. D. Ristovski[1]

[1] International Laboratory for Air Quality and Health, Queensland University of Technology,
Brisbane QLD 4000, Australia

Atmospheric Research, In press, corrected proof online, 2010

Statement of joint authorship

Title: Observation of the suppression of water uptake by marine particles

Authors: R. L. Modini, G. R. Johnson, C. He, Z. D. Ristovski

R. L. Modini

Contributed to experimental design and scientific method; developed concept for paper; conducted field work; analysed and interpreted the data; wrote manuscript

G. R. Johnson

Developed experimental design and scientific method; conducted field work; assisted with data interpretation; reviewed manuscript

C. He

Conducted field work and reviewed manuscript

Z. D. Ristovski

Developed experimental design and scientific method; contributed to concept development; conducted field work; assisted with data interpretation; reviewed manuscript

Abstract

A 4 week intensive measurement campaign was conducted in March–April 2007 at Agnes Water, a remote coastal site on the east coast of Australia. A Volatility-Hygroscopicity-Tandem Differential Mobility Analyser (VH-TDMA) was used to investigate changes in the hygroscopic properties of ambient particles as volatile components were progressively evaporated. Nine out of 18 VH-TDMA volatility scans detected internally mixed multi-component particles in the nucleation and Aitken modes in clean marine air. Evaporation of a volatile, organic-like component in the VH-TDMA caused significant increases in particle hygroscopicity. In 3 scans the increase in hygroscopicity was so large it was explained by an increase in the absolute volume of water uptake by the particle residuals, and not merely an increase in their relative hygroscopicity. This indicates the presence of organic components that were suppressing the hygroscopic growth of mixed particles on the timescale of humidification in the VH-TDMA (6.5 secs). This observation was supported by ZSR calculations for one scan, which showed that the measured growth factors of mixed particles were up to 18% below those predicted assuming independent water uptake of the individual particle components. The observed suppression of water uptake could be due to a reduced rate of hygroscopic growth caused by the presence of organic films or organic-inorganic interactions in solution droplets that had a negative effect on hygroscopicity.

Keywords: VH-TDMA; hygroscopic growth; organic films; marine aerosols

Introduction

Organic compounds can comprise a significant and sometimes dominant fraction of the atmospheric aerosol in all types of natural and polluted environments, including pristine marine environments (Blanchard, 1964; O'Dowd et al., 2004). Marine Organic Aerosol (OA) has both primary and secondary production mechanisms. The primary mechanism occurs when organic material concentrated at the ocean surface is collected by rising bubbles which subsequently burst to generate sea spray aerosol enriched with organic matter (Facchini et al., 2008; Keene et al., 2007; Modini et al., 2010). The secondary formation of marine OA results from the chemical processing of biogenic volatile organic compounds (BVOCs) into condensable organic vapours that subsequently enter the aerosol phase, probably through condensation rather than nucleation (O'Dowd and de Leeuw, 2007). Secondary marine OA formation is likely to occur frequently over coastal waters, where marine biota is often enriched. For example, marine OA has been indirectly observed in freshly nucleated particles (5–25 nm) at coastal sites on the west coast of Ireland (Vaattovaara et al., 2006) and on the east coast of Australia (Johnson et al., 2005; Modini et al., 2009).

The climatic impact of marine OA may be very large due to the fact it is being emitted or formed in the pristine marine boundary layer (MBL) where particle concentrations are relatively low (200–500 cm^{-3}) and the potential for the OA to effect marine cloud formation is, therefore, high. In order to assess the climatic impact of a marine OA source it is necessary to know how organic compounds affect the water uptake properties of atmospheric aerosol. Implicit in this understanding is knowledge of the mixing state of organic and inorganic components in the marine aerosol. In addition to affecting cloud condensation nuclei (CCN) concentrations, OA effects on hygroscopicity will also influence marine aerosol size, phase (Marcolli et al., 2004), radiative forcing (Randles et al., 2004), chemical reactivity and lifetime. This article will focus on sub-saturated hygroscopic measurements of OA (i.e. relative humidity (RH) < 100%).

Experimentally, the hygroscopic properties of a range of organic aerosols have been studied extensively over the last decade or so in the laboratory and the field. A thorough review of these studies is provided in section 7 of Kanakidou et al. (2005) and in Swietlicki et al. (2008). Depending on water solubility, organic compounds may or may not cause a significant reduction in the deliquescence relative humidity (DRH) of mixed organic-inorganic particles compared to purely inorganic particles. At higher RHs the hygroscopic growth factors of mixed (soluble or insoluble) organic-inorganic particles are lower than what would be expected for the inorganic components alone because measurements have so far indicated that organic aerosols are less hygroscopic than inorganic aerosols above deliquescence.

In general, this behaviour is adequately captured in state-of-the-art thermodynamic models that predict the hygroscopic properties of mixed organic-inorganic particles. This is despite the difficulty these models face in representing the physicochemical properties and non-ideality of the vast range of organic compounds potentially existing in atmospheric aerosol. To get around this issue, for example, some models rely on functional group contribution models for predicting the activity coefficients of organic compounds (e.g. UNIFAC: Fredenslund et al., 1975). There is also the issue of organic-inorganic interactions in aerosol solution droplets. Some models have explicitly treated organic-inorganic interactions that influence the water activity of the total solution droplet (Clegg et al., 2001; Erdakos et al., 2006; Ming and Russell, 2002; Zuend et al., 2008). However the development of these models is restricted by a lack of experimental data on relevant interaction parameters. This problem is avoided in models that assume a simple additive approach for the water activities of organic and inorganic components in solution (e.g. the ADDEM model: Topping et al., 2005). The assumption that inorganic and organic components in solution act independently of each other (i.e. no interactions) is known as the ZSR approximation (Chen et al., 1973; Stokes and Robinson, 1966).

Aside from its use in detailed thermodynamic models like ADDEM, the ZSR principle has been used to predict the hygroscopic growth of mixed particles from hygroscopic data for pure compounds (e.g. Brooks et al., 2004; Gysel et al., 2007; Meyer et al., 2009; Prenni et al., 2003). Comparisons between such ZSR-based predictions and measurements have indicated that the ZSR principle is frequently valid and therefore useful as a first order approximation. However, there are a few notable discrepancies. A number of laboratory based studies have found both positive and negative differences between measured and ZSR-predicted growth factors for mixed particles (Chan and Chan, 2003; Cruz and Pandis, 2000; Svenningsson et al., 2006; Zardini et al., 2008). These differences can be as large as 20% (Cruz and Pandis, 2000). Failure of the ZSR assumption indicates that interactions between organic and inorganic components have had an effect on the water activity of a solution droplet. For example the water solubility of some organic compounds can decrease/increase with increasing salt concentration in solution (salting out/salting in effects). Another intriguing interaction possibility is the formation of organic micelles capable of forming complex aggregates with inorganic cations, which effectively takes them out of solution (Tabazadeh, 2005).

In addition to affecting the equilibrium size of a mixed particle at a given RH (which may or may not be predictable with the ZSR principle), organic components can also affect the time that a particle requires to grow (or shrink) to this equilibrium size. These are so called kinetic or mass-transfer effects (Chan and Chan, 2005). Organic components that delay the hygroscopic growth of particles have been investigated in the laboratory (Chan and Chan, 2007; Sjogren et al., 2007) and observed in a small fraction (0–2%) of particles in a polluted, urban environment (Chuang, 2003). In the supersaturated regime, two recent field studies have observed delayed cloud droplet activation of mixed particles relative to ammonium sulphate particles (Ruehl et al., 2008; Shantz et al., 2010). Kinetic effects can potentially arise if an organic component is present as a film (Gill et al., 1983) or solid enclosure (Sjogren et al., 2007) that reduces the rate of water vapour transfer between the environment and soluble portion of a particle. These effects are important because they can affect the ability of particles to act as cloud condensation nuclei (CCN) due to the finite time available for particles to activate into cloud droplets in a rising air mass. This in turn can affect cloud microphysical properties (Chuang et al., 1997; Feingold and Chuang, 2002).

A promising method for investigating the hygroscopic properties of mixed organic-inorganic particles in the field and the laboratory is the Volatility Hygroscopicity- Tandem Differential Mobility Analyser (VH-TDMA) (Johnson et al., 2004). This technique is able to probe changes in the hygroscopic properties of particles as volatile organic components are progressively evaporated (Fletcher et al., 2007; Johnson et al., 2005; Meyer et al., 2009; Meyer and Ristovski, 2007; Ristovski et al., 2010; Sellegri et al., 2008; Villani et al., 2009). For example in the ambient study of Johnson et al. (2005), increases in the hygroscopic growth factors (HGF) at 84–92% RH of marine particles in the nucleation, Aitken and accumulation modes were observed after the removal of volatile organic species. Furthermore, the authors calculated that the changes in HGF were explained by an increase in the absolute amount of water uptake by the residuals, and not merely an increase in their hygroscopicity. This result indicates that there was a real suppression of water uptake by the marine OA component on the timescale of humidification in the VH-TDMA system employed in that study (5-10s). This observation of water uptake suppression may have occurred due to negative organic-inorganic interactions in solution (e.g. ‘salting out’ effect) or kinetic effects (e.g. organic film formation).

In this paper we report new observations of water uptake suppression by marine particles. These observations were made with a VH-TDMA during a measurement campaign conducted at the remote coastal location of Agnes Water on the east coast of Australia.

Materials and Methods

Campaign details

A month-long measurement campaign was conducted in March–April 2007 at Agnes Water (24.2° S 151.9° W) on the east coast of Australia. The campaign and measurement site are described in detail in (Modini et al., 2009). This paper also describes the frequent new particle formation events observed during the campaign and uses VH-TDMA data to conclude that the condensation of sulphate and/or organic vapours was responsible for driving particle growth at sizes greater than 10 nm during the events. The Agnes Water site has a large open ocean sector covering the range of bearings from 320–110°. A large sand island (Fraser Island) covered in vegetation lies 150 km away at a bearing of 110–135°. In between there are the shallow (depth < 25 m), biologically-rich waters of Hervey Bay. Further south at a bearing of 140° is the town of Bundaberg. The southernmost reefs of the Great Barrier Reef (GBR) are approximately 50 km away at a bearing of 050°. SE-trade winds blew very consistently during the campaign and these carried air masses for at least 4 days over the open ocean SE of our sampling site. A regular land-sea breeze effect meant that, in general, continentally affected air masses reached the site during the night and early morning (average particle number concentration between 4 and 165 nm as measured by an SMPS ($N_{4\text{–}165nm}$) = 587 cm^{-3}), while marine air masses reached the site during the day and evening (Average $N_{4\text{–}165nm}$ = 345 cm^{-3}). The measurements presented here were all obtained under marine sampling conditions, which were defined as time periods of greater than 4 hrs when wind direction was in the sector 320–135° and particle number concentration ($N_{4\text{–}165nm}$) was less than 400 cm^{-3} (unless a particle nucleation event was occurring, see Modini et al. (2009)).

Volatility Hygroscopic- Tandem Differential Mobility Analyser (VH-TDMA)

Instrument description

The VH-TDMA consists of an electrostatic classifier that preselects particles of a given mobility diameter (10–110 nm), followed by a purpose built thermodenuder that heats the particles to a given temperature (ambient–600°C), and then a humidifier (Johnson et al., 2008) that operates from 5–95% RH. Particle residence time in the thermodenuder is <1 sec and in the humidifier is 6.5 secs. Scanning mobility particle sizers (SMPSs) are placed after both the heating and humidification stages to examine any size changes resulting from these conditioning steps. Raw SMPS data were inverted with the TDMAinv algorithm (Gysel et al., 2009). Thus, the output variables of the VH-TDMA are chosen initial particle diameter (d_i), particle diameter after volatilisation (d_v) and particle diameter after volatilisation *and* subsequent humidification (d_{vh}). Hygroscopic growth factor ($HGF=d_{vh}/d_v$) and volume fraction remaining ($V/Vo=(d_v/d_i)^3$) are calculated directly from these variables. Assuming an SMPS sizing accuracy of ±1% and RH uncertainty of ±1.1% the theoretical uncertainty (95% confidence level) is ±3% for V/Vo and ±3% for HGF at 90% RH.

A number of deliquescence scans were performed with the VH-TDMA during the campaign. In this mode of operation the thermodenuder was set to ambient temperature and the RH in the humidifier was continually ramped from X to 90% RH. A HGF measurement was taken for every 1% change in RH. Volatility scans were also performed with the VH-TDMA. In this mode of operation the humidifier was kept at a constant RH of 90% (with ±0.5% precision) while thermodenuder temperature was increased in discrete 5–10°C steps until complete particle evaporation occurred. HGF at 90% RH ($HGF_{90\%}$) and V/Vo were measured at each thermodenuder temperature resulting in a total VH-TDMA scan time of ~1–2 hrs. The purpose of the volatility scanning procedure was to indirectly probe the chemical composition of ambient marine particles and to observe the change in $HGF_{90\%}$ as volatile components were progressively removed from these particles.

It is possible to make inferences regarding chemical composition from VH-TDMA volatility scans because the volatile and hygroscopic properties of particles are determined by their chemical composition. Single TDMA techniques (e.g. VTDMA or HTDMA) are limited in their ability to infer composition by the fact that different chemical species can display similar physical properties (i.e. volatility or hygroscopicity is a non-unique function of chemical composition). The VH-TDMA addresses this problem by simultaneously measuring the volatile and hygroscopic properties of particles. This combined TDMA approach significantly constrains the list of potential chemical species within atmospheric nanoparticles. An example of how chemical composition can be inferred from VH-TDMA data is supplied in Modini et al. (2009), where the VH-TDMA was used to investigate the composition of nucleation mode particles.

Data analysis– Water Uptake Ratio (WUR)

In order to investigate any possibility of suppressed hygroscopic growth by volatile components we examine a variable called Water Uptake Ratio (WUR). This variable was first applied to VH-TDMA data by Johnson et al. (2005). In that paper it was introduced as β_w. WUR is defined as the ratio of water volume uptake of residual particles to the water volume uptake of untreated particles. Two forms of calculating WUR using output variables of the VH-TDMA are given in equation 1, where the subscript zero refers to variables measured with the thermodenuder set to ambient temperature.

$$WUR = \frac{\left(d_{vh}^3 - d_v^3\right)}{\left(d_{vh,o}^3 - d_i^3\right)} = \frac{V}{V_o}\cdot\frac{\left(HGF^3 - 1\right)}{\left(HGF_o^3 - 1\right)} \qquad (1)$$

WUR is sensitive to changes in particle diameter due to the cubic dependences in equation 1. Assuming an SMPS sizing accuracy of ±1% and RH uncertainty of ±1.1% we estimate the theoretical uncertainty (95% confidence level) in WUR as

±20%. At temperatures where volatile components have evaporated, WUR greater than 1 indicates that the absolute water uptake of the residual is greater than that of the untreated particle despite the reduction in overall particle volume. This would indicate that a volatile component was suppressing the hygroscopic growth of the untreated particle on the timescale of humidification in the VH-TDMA.

To illustrate this in more detail let us consider a hypothetical example of an internally mixed particle consisting of a hygroscopic inorganic component (e.g. ammonium sulphate) and a non-hygroscopic, volatile organic component. At 90% RH the mixed particle will uptake a certain volume of water, which can be entirely attributed to the inorganic portion of the particle since the organic component is assumed non-hygroscopic. Let us further assume that if the mixed particle is heated to 100°C the volatile organic particle mass evaporates completely while the inorganic mass remains constant. Two possibilities then arise. They are illustrated in Fig. 4.1. In this figure we have plotted WUR, HGF, V/Vo, and the hygroscopic growth factors of the two individual components as a function of the thermodenuder temperature. Firstly, if the organic component is not suppressing the water uptake of the inorganic component (left column, Fig. 4.1) than the water uptake of the particle will remain constant even when the organic component has been evaporated at 100°C. This is because the inorganic mass and the hygroscopic growth factor of the inorganic (and therefore water associated with it) have not changed. In this case WUR above 100°C will equal 1. However, $HGF_{90\%}$ will still increase because the reference diameter (the denominator in the HGF definition, d_v) has decreased due to the reduction in particle mass associated with the evaporation of the organic component while the soluble (inorganic) mass has remained constant.

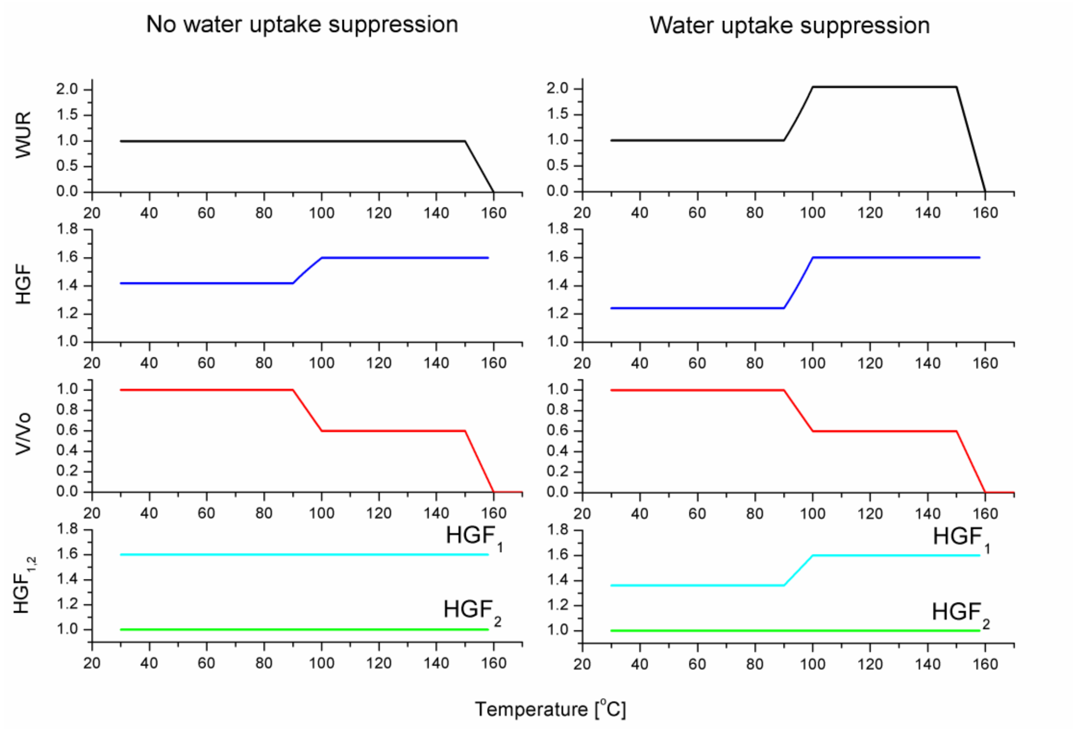


Figure 4.1: Calculated values of WUR, $HGF_{90\%}$ and V/Vo as well as the HGF's of the 2 components $HGF_{1,2}$ (cyan, HGF_1: inorganic and green, HGF_2: organic). We have assumed that the particle consists of 40% organic, 60% inorganic. The graphs on the left hand side present the case where there is no interaction between the organic and inorganic and therefore no suppression of growth. For the graphs on the right hand side we have assumed that the presence of organics causes a 15% suppression of growth and this is illustrated by an apparent reduction in HGF_1.

Let us now consider the second possibility that the volatile organic component is somehow suppressing the water uptake of the inorganic component (right column, Fig. 4.1). We have illustrated this as an apparent reduction in the HGF of the inorganic component when the organic component is present. In this case, when the organic component is removed at 100°C the apparent HGF and the volume of water taken up by the inorganic component will increase. Therefore, the volume of water taken up by the mixed particle will be greater above 100°C than at ambient temperature. This means WUR will be greater than 1. It is important to note that in both cases described in our hypothetical example evaporation of the organic component will be followed by an increase in $HGF_{90\%}$. However, only in the water uptake suppression case does WUR become greater than 1. This is why it is a useful variable for identifying water uptake suppression. We also point out that when the inorganic component evaporates at higher temperatures WUR always approaches 0 because it is proportional to V/Vo (Equation 1). Physically this occurs because the amount of soluble material is decreasing with temperature, and therefore the water associated with it also decreases.

Results and Discussion

Typical VH-TDMA scans

A total of 18 volatility scans were conducted during the campaign under marine sampling conditions. Two main categories of particle type emerged from this data. Nine volatility scans showed a one-step volatilisation process. An example of this type of scan for 32 nm particles is shown in Fig. 4.2A. This scan was conducted on 23 March 2007 from 10:51 to 11:48. Particle volatilisation was relatively discrete and occurred in the temperature range 150–200°C; although a small reduction in particle volume was observed before this. Simultaneously measured $HGF_{90\%}$ was relatively constant throughout the scan. Also plotted in Fig. 4.2 is a volatility curve of 29 nm laboratory generated ammonium sulphate particles and a modelled, dry-size dependent ammonium sulphate $HGF_{90\%}$ curve. In this paper all theoretical ammonium sulphate growth factors are calculated using the model of Biskos et al. (2006). The similarity between the ambient data and the laboratory-measured and modelled data for ammonium sulphate particles leads us to suggest that the ambient particles are composed primarily of ammoniated sulphates (partially to fully neutralised sulphuric acid). We cannot judge the degree of neutralisation purely from this volatility scan because different forms of ammoniated sulphates have similar volatility curves and hygroscopic properties at 90% RH.

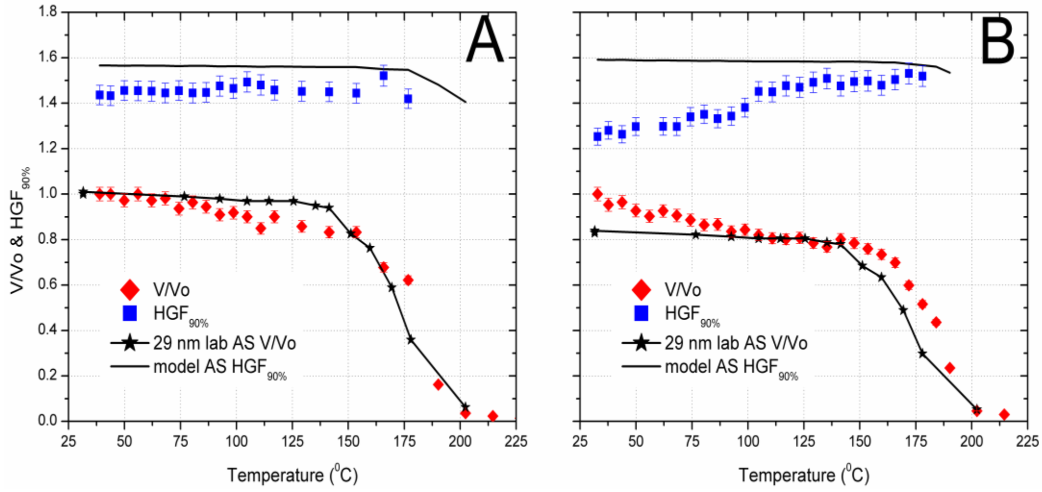


Figure 4.2: VH-TDMA volatility scans displaying V/Vo (diamonds), HGF at 90% RH (squares), a measured volatility (V/Vo) curve for 29 nm ammonium sulphate (AS) particles generated in the laboratory (stars with black line) and modelled, dry-size dependant AS $HGF_{90\%}$ curve (straight black line). Error bars represent ±3% theoretical uncertainty in V/Vo and $HGF_{90\%}$. **A:** 32 nm particles sampled from 10:51 to 11:48 on 23 March 2007. **B:** 40 nm particles sampled from 11:08 to 12:18 on 4 April 2007. In panel **B** the volatility curve for the laboratory generated AS particles has been normalised to the apparent volume fraction of the more hygroscopic particle component.

To further examine particle chemical composition on the morning of 23 March 2007 we present a deliquescence scan for 32 nm particles in Fig. 4.3. This scan was conducted from 09:30 to 10:47, immediately prior to the volatility scan shown in Fig. 4.2A. The stability of the meteorological parameters (e.g. average wind direction = 107.4 ± 2.3° (1 standard deviation)) and particle concentration (average $N_{4–165nm}$ = 183 ± 36 cm^{-3}) during this morning indicated that we were sampling from the same marine air mass in both scans. Particle deliquescence was abrupt and occurred at ~80% RH. This is consistent with laboratory measurements of 79 ± 2.5% DRH for ammonium sulphate nanoparticles (Biskos et al., 2006). This suggests that the majority of the 32 nm particles sampled on the morning of 23 March 2007 can indeed be identified as ammoniated sulphates. Furthermore the abrupt deliquescence near 80% RH indicates that the sulphate was in its most neutralised form, ammonium sulphate. However, it is important to note that particle growth was observed before deliquescence and particle growth factors following deliquescence were significantly below expected values

(Fig. 4.2A and 4.3). This indicates that there were certainly species other than ammonium sulphate also present in the aerosol in small amounts.

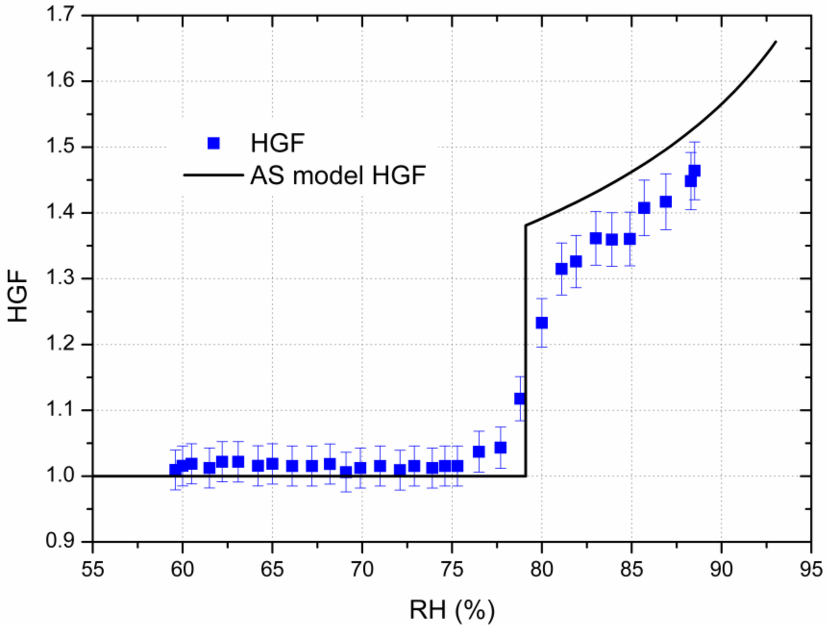


Figure 4.3: Deliquescence scan conducted with the VH-TDMA from 09:30 to 10:47 on 23 March 2007. Selected particle size was 32 nm.

The other 9 out of 18 VH-TDMA volatility scans completed during the campaign showed particles with a multi-step volatilisation process. For these scans particles were sampled from a nucleation or an Aitken mode (initial particle size = 17–42 nm). A typical example of one of these scans is shown in Fig. 4.2B. This scan was conducted on 40 nm particles from 11:08 to 12:18 on 4 April 2007. The particles exhibited a distinct two-step volatilisation process and corresponding change in HGF, which means they contained two significant components of differing volatility and hygroscopicity. The first component was relatively volatile; it completely evaporated by 110^{0}C where the volatility curve flattened out. Evaporation of this component caused an increase in HGF$_{90\%}$, which indicates that it was non- or only slightly-hygroscopic. These combined properties suggest that this component was most likely organic. After evaporation of the organic component the HGF$_{90\%}$ and volatility curve of the second component (residual particles) corresponded well to modelled, dry-size dependent ammonium sulphate HGF$_{90\%}$ values and the normalised laboratory measured, 29nm ammonium sulphate volatility curve (both plotted in Fig. 4.2B). Therefore this component was most likely the ammoniated sulphate species observed in the single-step volatility scans described above and shown in Fig. 4.2A. Unfortunately no corresponding deliquescence scans were conducted for the mixed organic-sulphate particles so we cannot judge what effect the extra, volatile organic component had on the deliquescence relative humidity of the mixed particles. The volume fraction of the organic component when present was generally less than 20% but did reach 40% during one scan (see Figure 9 of Modini et al., 2009). It should also be noted that all mixed particles referred to here were internal mixtures as evidenced by the fact only single modes were observed in the size distributions after volatilisation and/or humidification.

Water uptake suppression

Water uptake ratio (WUR) was calculated as a function of thermodenuder temperature for all the VH-TDMA volatility scans. Of the 9 scans that indicated mixed particles (multi-step volatilisation), 3 scans on 2 separate days contained WUR values significantly greater than 1. These scans are displayed in Fig. 4.4 and the caption to this figure details the times and dates when these scans were completed. In all 3 scans a volatile component evaporated from the particles at temperatures below 100°C. Evaporation of this volatile component caused an increase in both $HGF_{90\%}$ and WUR. As explained above, if the evaporation of a volatile component results in WUR increasing significantly above 1, than that component was causing suppression of hygroscopic growth. The highest WUR values were achieved during the scan completed from 11:08 to 12:18 on 4 April 2007 (Fig. 4.4A). Here WUR reached a maximum value of 1.9 from 130–154°C. Physically this means the volume of water taken up by the sulphate residuals following heating in this temperature range was almost twice the volume taken up by the same sulphate component in the untreated particles.

To further explore the suppression of hygroscopic growth of particles sampled from 11:08 to 12:18 on 4 April 2007 (Fig. 4.2B and Fig. 4.4A) we compared measured and ZSR-predicted $HGF_{90\%}$ for this scan in Fig. 4.5. Under the ZSR

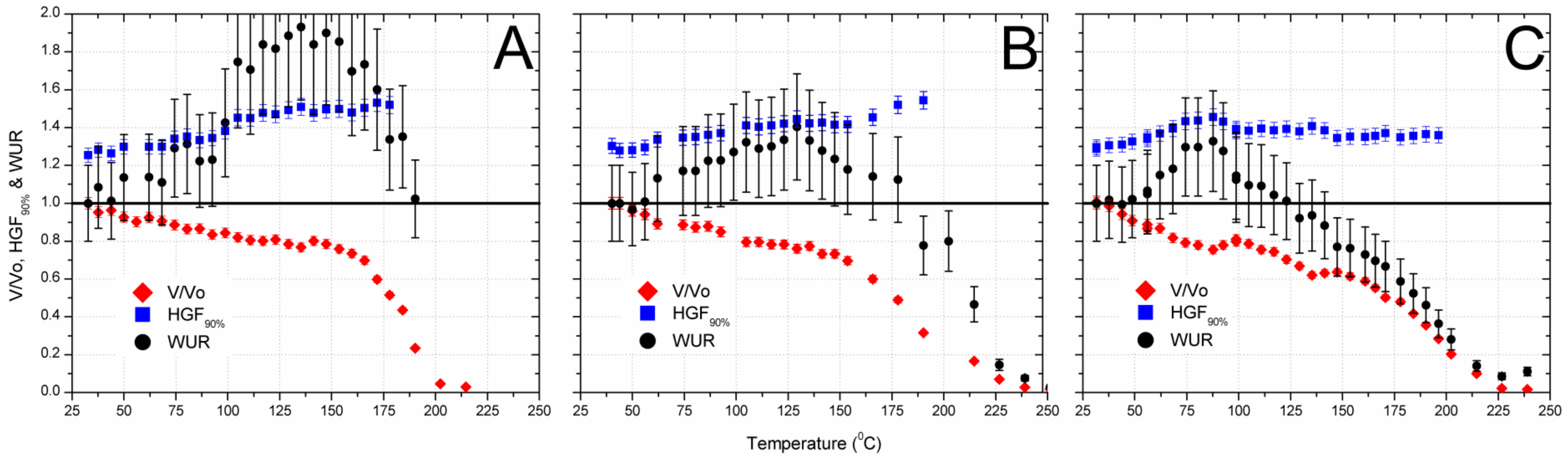


Figure 4.4: VH-TDMA volatility scans displaying V/Vo (diamonds), $HGF_{90\%}$ (squares) and WUR (circles) as a function of thermodenuder temperature. Error bars represent theoretical uncertainties: ±20% for WUR and ±3% for V/Vo and $HGF_{90\%}$. **A:** 40 nm particles sampled from 11:08 to 12:18 on 4 April 2007. **B:** 40 nm particles sampled from 13:25 to 14:42 on 4 April 2007. **C:** 42 nm particles sampled from 16:11 to 17:38 on 8 April 2007.

approximation the HGF of a mixed particle can be calculated by the volume-fraction-weighted sum of the HGF's of individual components in that particle. In order to apply this approximation we assumed particles were composed of only organics and ammonium sulphate and that at 110°C all of the organics and none of the ammonium sulphate had evaporated from the particles. We also assumed that the organic component was non-hygroscopic at 90% RH (i.e. $HGF_{org} = 1$). The volume fraction of organics for input into the ZSR model was calculated as a function of temperature from the volatility curve, V/Vo in Fig. 4.2B. Initial organic volume fraction (i.e. at ambient temperature) was 17%. For ammonium sulphate HGFs we used theoretical values calculated at 90% RH and the same dry size as the mixed particle.

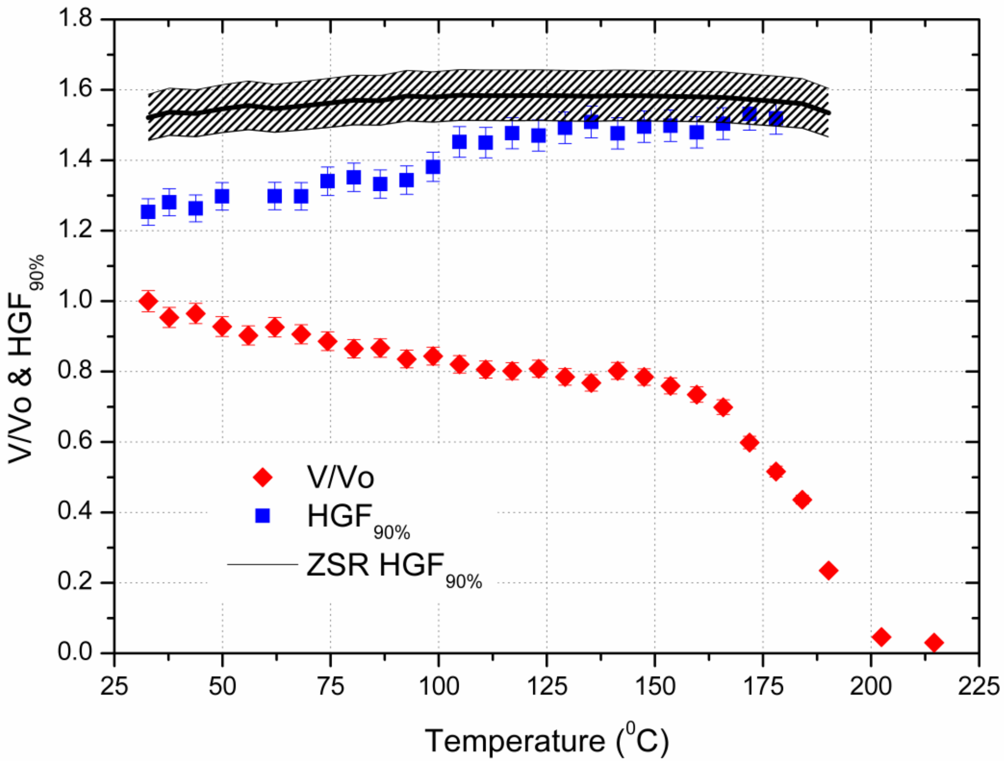


Figure 4.5: VH-TDMA volatility scan of 40 nm particles completed from 11:08 to 12:18 on 4 April 2007. This scan is also shown in Figure 4.2B and 4.4A. This time we have also plotted ZSR-predicted HGF values as a function of temperature. The shaded area surrounding the ZSR HGF curve represents the 99% confidence interval of our predictions.

The measured $HGF_{90\%}$ was significantly smaller than the ZSR-predicted $HGF_{90\%}$ at lower temperatures where the organic component was still present. For example at ambient temperature the measured $HGF_{90\%}$ (1.25 ± 0.04) was 18% below the predicted $HGF_{90\%}$ (1.52 ± 0.07). Even allowing for the simplicity of our ZSR model this result is consistent with WUR values greater than 1. Both analyses indicated that a volatile organic component can significantly suppress the hygroscopic growth of atmospheric particles on the 6.5 sec timescale of humidification in the VH-TDMA.

Possible mechanisms of water uptake suppression

Based on the data collected here we cannot conclusively determine the mechanism behind the observed suppression of water uptake. However we can explore 2 possibilities. Firstly the organic components that suppressed hygroscopic growth may have existed as organic films coating inorganic cores. Such films can potentially inhibit the rate of water vapour transfer between particles and their surroundings (Chuang, 2003; Donaldson and Vaida, 2006; Gill et al., 1983) and particles may have had too little time to grow to their equilibrium size in the humidification section of the VH-TDMA (Chan and Chan, 2005). Amphiphilic compounds are good film-forming compounds because they consist of a hydrophilic polar head and a hydrophobic tail (e.g. long-chain carboxylic acids). The resulting insolubility causes these compounds to congregate at air-water interfaces with their heads pointing into solution and their tails exposed to the air. Soluble compounds are also capable of forming organic films (e.g. ethanol). In this case the film refers to the spontaneous, preferential partitioning of soluble compounds to the surface compared to the bulk solution. Only insoluble organic films are capable of significantly impeding water vapour transport so these are the type of films that must have been present if this mechanism can explain our observation of water uptake suppression.

In the marine environment amphiphilic compounds are found in the sea-surface microlayer in biologically active waters and they can form coats on sea-salt particles produced during the bubble-bursting process (Ellison et al., 1999; Tervahattu et al., 2002a; Tervahattu et al., 2002b). However, we detected water-uptake-suppressing organic compounds internally mixed with sulphates. Sulphates are formed secondarily in the marine atmosphere (Fitzgerald, 1991) and therefore these organic compounds are almost certainly also secondarily formed. Organic components were detected in particles that had travelled for 3-4 days over the open ocean; possibly crossing the vegetation covered Fraser Island before arriving at our sampling point. Any source of secondary film-forming organic compounds would need to be within this air mass back trajectory.

One possible source is monoterpene emission from Fraser Island. Anttila et al. (2007) have provided evidence from chamber studies that indicates the ozonolysis products from monoterpenes can form insoluble films on aqueous sulphate seeds. Furthermore, the uptake probability of N_2O_5 by the coated particles was observed to decrease by up to an order of magnitude relative to the uncoated aqueous seeds (Anttila et al., 2006; Folkers et al., 2003). While this is proof that the films could reduce the uptake of reactive species (N_2O_5), no observational evidence was provided to suggest they could reduce the uptake of non-reactive species like water. Based on only a 10–30% reduction in N_2O_5 uptake probability for films formed from the oxidation products of a mixture of 4 monoterpenes, doubts were also expressed about the ability of atmospheric organic compounds, which are many and varied, to form condensed organic films. Depending on surface area per molecule, organic films can exist in expanded (gaseous or liquid-expanded) or condensed states. Organic molecules with long, straight carbon chains are favoured to form condensed films because they can pack closely together. On the other hand, bent molecules and the complex mixtures of organic compounds that are likely to exist in the atmosphere are less likely to pack closely together and may only be capable of forming expanded films. In order to achieve significant retardation of water vapour transfer organic films must be in the condensed state (Donaldson and Vaida, 2006; Gill et al., 1983).

We have previously used our VH-TDMA to investigate sulphate particles internally mixed with an organic component derived from the photo-oxidation of monoterpenes in a chamber study (Meyer et al., 2009) and a field study in a eucalypt forest (Ristovski et al., 2010). No evidence was obtained in either of these studies for the suppression of hygroscopic growth at RH above 85%. This suggests that in these instances if photo-oxidised monoterpene products did form organic films, the films did not inhibit water uptake on a 6.5 sec timescale. Nevertheless, taking all these considerations into account, it is still a possibility that organic films derived from processed vegetation emissions from Fraser Island introduced kinetic effects into the VH-TDMA measurements reported here.

The second possibility is that $HGF_{90\%}$ was measured at equilibrium (i.e. no kinetic effects) but the equilibrium sizes of the mixed particles at 90% RH were actually up to 18% below what was predicted by the ZSR approximation. Cruz and Pandis (2000) observed positive and negative discrepancies of this magnitude when comparing ZSR predictions with HTDMA measurements of laboratory generated pinoic acid-ammonium sulphate (AS), pinoic acid-sodium chloride (NaCl) and glutaric acid-NaCl particles. Similarly Svenningson et al. (2006) measured growth factors 15% below ZSR predictions for laboratory generated succinic acid (10%)-fulvic acid (10%)-AS (50%)-NaCl (30%) particles. These discrepancies can occur due to organic-inorganic interactions in solution that affect the water activity of a solution droplet (e.g. salting out effect, complex aggregate formation). It should be noted that many studies have found good agreement between measured and ZSR-predicted growth factors at 90% RH (e.g. Meyer et al., 2009; Topping et al., 2005). Nevertheless, negative organic-inorganic interactions in solution could still explain the observed water uptake suppression.

Conclusion

During an intensive month-long measurement campaign at Agnes Water 9 out of 18 VH-TDMA scans indicated the presence of internally mixed, multi-component particles in the nucleation and Aitken modes of clean marine air. For 3 of these 9 scans evaporation of a volatile organic component in the VH-TDMA caused significant increases in $HGF_{90\%}$ and water uptake ratio (WUR). This meant that the absolute volume of water taken up by the residuals was greater than the volume of water taken up by the same components when mixed with the volatile organic components. In addition, ZSR calculations for one of the scans indicated that measured $HGF_{90\%}$ values were up to 18% below those predicted assuming independent water uptake of individual components in the mixed particles. These two streams of analyses indicated that we observed organic components that significantly suppressed the water uptake of mixed particles. We suggest two possible mechanisms that could explain the observed water uptake suppression: organic film formation or complex interactions between organic and inorganic components in solution. Further research is required to determine which of these two mechanisms is most relevant, and to investigate the identities and abundance of hygroscopic growth inhibiting organic compounds in natural and polluted environments.

Acknowledgements

This work was funded by the International Laboratory for Air Quality and Health.

References

Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the Reactive Uptake of Gaseous Compounds by Organic-Coated Aqueous Aerosols: Theoretical Analysis and Application to the Heterogeneous Hydrolysis of N2O5, J. Phys. Chem. A, 110, 10435-10443, 10.1021/jp062403c, 2006.

Anttila, T., Kiendler-Scharr, A., Mentel, T. F., and Tillmann, R.: Size dependent partitioning of organic material: evidence for the formation of organic coatings on aqueous aerosols J. Atmos. Chem., 57, 215-237, 10.1007/s10874-007-9067-9, 2007.

Biskos, G., Paulsen, D., Russell, L. M., Buseck, P. R., and Martin, S. T.: Prompt deliquescence and efflorescence of aerosol nanoparticles, Atmos. Chem. Phys., 6, 4633-4642, 2006.

Blanchard, D. C.: Sea-to-Air transport of surface active material, Science, 146, 396-397, 1964.

Brooks, S. D., DeMott, P. J., and Kreidenweis, S. M.: Water uptake by particles containing humic materials and mixtures of humic materials with ammonium sulfate, Atmos. Env., 38, 1859-1868, 2004.

Chan, M. N., and Chan, C. K.: Hygroscopic Properties of Two Model Humic-like Substances and Their Mixtures with Inorganics of Atmospheric Importance, Env. Sci. Tech., 37, 5109-5115, 10.1021/es034272o, 2003.

Chan, M. N., and Chan, C. K.: Mass transfer effects in hygroscopic measurements of aerosol particles, Atmos. Chem. Phys., 5, 2703-2712, 2005.

Chan, M. N., and Chan, C. K.: Mass transfer effects on the hygroscopic growth of ammonium sulfate particles with a water-insoluble coating, Atmos. Env., 41, 4423-4433, 2007.

Chen, H., Sangster, J., Teng, T. T., and Lenzi, F.: A general method of predicting the water activity of ternary aqueous solutions from binary data, Can. J. Chem. Eng., 51, 234-241, 1973.

Chuang, P. Y., Charlson, R. J., and Seinfeld, J. H.: Kinetic limitations on droplet formation in clouds, Nature, 390, 594–596, 1997.

Chuang, P. Y.: Measurement of the timescale of hygroscopic growth for atmospheric aerosols, J. Geophys. Res., 108(D9), 4282, 10.1029/2002jd002757, 2003.

Clegg, S. L., Seinfeld, J. H., and Brimblecombe, P.: Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds, J. Aer. Sci., 32, 713-738, 2001.

Cruz, C. N., and Pandis, S. N.: Deliquescence and Hygroscopic Growth of Mixed Inorganicâ˘’Organic Atmospheric Aerosol, Env. Sci. Tech., 34, 4313-4319, 10.1021/es9907109, 2000.

Donaldson, D. J., and Vaida, V.: The Influence of Organic Films at the Air-Aqueous Boundary on Atmospheric Processes, Chem. Rev., 106, 1445-1461, 10.1021/cr040367c, 2006.

Ellison, G. B., Tuck, A. F., and Vaida, V.: Atmospheric processing of organic aerosols, J. Geophys. Res., 104(D9), 11,633–611,641, 10.1029/1999jd900073, 1999.

Erdakos, G. B., Chang, E. I., Pankow, J. F., and Seinfeld, J. H.: Prediction of activity coefficients in liquid aerosol particles containing organic compounds, dissolved inorganic salts, and water--Part 3: Organic compounds, water, and ionic constituents by consideration of short-, mid-, and long-range effects using X-UNIFAC.3, Atmos. Env., 40, 6437-6452, 2006.

Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, L17814, doi:10.1029/2008GL034210, 2008.

Feingold, G., and Chuang, P. Y.: Analysis of the influence of filmforming compounds on droplet growth: Implications for cloud microphysical processes and climate, J. Atmos. Sci., 59, 2006-2018, 2002.

Fitzgerald, J. W.: Marine aerosols: A review, Atmos. Env., 25, 533-545, 1991.

Fletcher, C. A., Johnson, G. R., Ristovski, Z. D., and Harvey, M.: Hygroscopic and volatile properties of marine aerosol observed at Cape Grim during the P2P campaign, Environ. Chem., 4, 162-171, 2007.

Folkers, M., Mentel, T. F., and Wahner, A.: Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N2O5, Geophys. Res. Lett., 30 (12), 1644, 10.1029/2003gl017168, 2003.

Fredenslund, A., Jones, R. L., and Prausnitz, J. M.: Group-contribution estimation of activity coefficients in nonideal liquid mixtures, AIChE, 21, 1086-1099, 1975.

Gill, P. S., Graedel, T. E., and Weschler, C. J.: Organic Films on Atmospheric Aerosol Particles, Fog Droplets, Cloud Droplets, Raindrops, and Snowflakes, Rev. Geophys., 21(4), 903–920, 10.1029/RG021i004p00903, 1983.

Gysel, M., Crosier, J., Topping, D. O., Whitehead, J. D., Bower, K. N., Cubison, M. J., Williams, P. I., Flynn, M. J., McFiggans, G. B., and Coe, H.: Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2, Atmos. Chem. Phys., 7, 6131-6144, 2007.

Gysel, M., McFiggans, G. B., and Coe, H.: Inversion of tandem differential mobility analyser (TDMA) measurements, J. Aerosol Sci., 40, 134-151, 2009.

Johnson, G. R., Ristovski, Z., and Morawska, L.: Method for measuring the hygroscopic behaviour of lower volatiliy fractions in an internally mixed aerosol, J. Aer. Sci., 35, 443-455, 2004.

Johnson, G. R., Ristovski, Z. D., D'Anna, B., and Morawska, L.: Hygroscopic behaviour of partially volatilised coastal marine aerosols using the volatilisation and humidification tandem differential mobility analyser technique, J. Geophys. Res., 110, D20203, doi:10.1029/2004JD005657, 2005.

Johnson, G. R., Fletcher, C., Meyer, N., Modini, R., and Ristovski, Z. D.: A robust, portable H-TDMA for field use, J. Aer. Sci., 39, 850-861, 2008.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, 2005.

Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl, E. E., Izaguirre, M. A., Davis, A. J., Long, M. S., Zhou, X., Smoydzin, L., and Sander, R.: Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface, J. Geophys. Res., 112, D21202, doi:10.1029/2007JD008464, 2007.

Marcolli, C., Luo, B., and Peter, T.: Mixing of the Organic Aerosol Fractions: Liquids as the Thermodynamically Stable Phases, J. Phys. Chem. A, 108, 2216-2224, 2004.

Meyer, N. K., and Ristovski, Z. D.: Ternary Nucleation as a Mechanism for the Production of Diesel Nanoparticles: Experimental Analysis of the Volatile and Hygroscopic Properties of Diesel Exhaust Using the Volatilization and Humidification Tandem Differential Mobility Analyzer, Environ. Sci. Tech., 41, 7309-7314, 10.1021/es062574v, 2007.

Meyer, N. K., Duplissy, J., Gysel, M., Metzger, A., Dommen, J., Weingartner, E., Alfarra, M. R., Prevot, A. S. H., Fletcher, C., Good, N., McFiggans, G., Jonsson, Å. M., Hallquist, M., Baltensperger, U., and Ristovski, Z. D.: Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and unseeded SOA particles, Atmos. Chem. Phys., 9, 721-732, 2009.

Ming, Y., and Russell, L. M.: Thermodynamic equilibrium of organic-electrolyte mixtures in aerosol particles, AIChE, 48, 1331-1348, 2002.

Modini, R. L., Harris, B., and Ristovski, Z. D.: The organic fraction of bubble-generated, accumulation mode Sea Spray Aerosol (SSA), Atmos. Chem. Phys., 10, 2867-2877, 2010.

Modini, R. L., Ristovski, Z. D., Johnson, G. R., He, C., Surawski, N., Morawska, L., Suni, T., and Kulmala, M.: New particle formation and growth at a remote, sub-tropical coastal location, Atmos. Chem. Phys., 9, 7607-7621, 2009.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J.-P.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676-680, 2004.

O'Dowd, C. D., and de Leeuw, G.: Marine aerosol production: a review of the current knowledge, Phil. Trans. R. Soc. A, 365, 1753-1774, 10.1098/rsta.2007.2043, 2007.

Prenni, A. J., DeMott, P. J., and Kreidenweis, S. M.: Water uptake of internally mixed particles containing ammonium sulfate and dicarboxylic acids, Atmos. Env., 37, 4243-4251, 2003.

Randles, C. A., Russel, L. M., and Ramaswamy, V.: Hygroscopic and optical properties of organic sea salt aerosol and consequences for climate forcing, Geophys. Res. Lett., 31, L16108, doi:10.1029/2004GL020628, 2004.

Ristovski, Z. D., Suni, T., Kulmala, M., Boy, M., Meyer, N. K., Duplissy, J., Turnipseed, A., Morawska, L., and Baltensperger, U.: The role of sulphates and organic vapours in new particle formation in a eucalypt forest, Atmos. Chem. Phys., 10, 2919-2926, 2010.

Ruehl, C. R., Chuang, P. Y., and Nenes, A.: How quickly do cloud droplets form on atmospheric particles?, Atmos. Chem. Phys., 8, 1043-1055, 2008.

Sellegri, K., Villani, P., Picard, D., Dupuy, R., O'Dowd, C., and Laj, P.: Role of the volatile fraction of submicron marine aerosol on its hygroscopic properties, Atmos. Res., 90, 272-277, 2008.

Shantz, N. C., Chang, R. Y.-W., Slowik, J. G., Abbatt, J. P. D., and Leaitch, W. R.: Slower CCN growth kinetics of anthropogenic aerosol compared to biogenic aerosol observed at a rural site, Atmos. Chem. Phys., 10, 299-312, 2010.

Sjogren, S., Gysel, M., Weingartner, E., Baltensperger, U., Cubison, M. J., Coe, H., Zardini, A. A., Marcolli, C., Krieger, U. K., and Peter, T.: Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures, J. Aer. Sci., 38, 157-171, 2007.

Stokes, R. H., and Robinson, R. A.: Interactions in Aqueous Nonelectrolyte Solutions. I. Solute-Solvent Equilibria, J. Phys. Chem., 70, 2126-2131, 1966.

Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S., Zhou, J., Mønster, J., and Rosenørn, T.: Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance, Atmos. Chem. Phys., 6, 1937-1952, 2006.

Swietlicki, E., Hansson, H.-C., HÄMeri, K., Svenningsson, B., Massling, A., Mcfiggans, G., Mcmurry, P. H., PetÄJÄ, T., Tunved, P., Gysel, M., Topping, D. O., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., and Kulmala, M.: Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments: a review, Tellus B, 60, 432-469, 2008.

Tabazadeh, A.: Organic aggregate formation in aerosols and its impact on the physicochemical properties of atmospheric particles, Atmos. Env., 39, 5472-5480, 2005.

Tervahattu, H., Hartonen, K., Kerminen, V.-M., Kupiainen, K., Aarnio, P. i., Koskentalo, T., Tuck, A. F., and Vaida, V.: New evidence of an organic layer on marine aerosols, J. Geophys. Res., 107(D7), 4053, 10.1029/2000jd000282, 2002a.

Tervahattu, H., Juhanoja, J., and Kupiainen, K.: Identification of an organic coating on marine aerosol particles by TOF-SIMS, J. Geophys. Res., 107(D16), 4319, 10.1029/2001jd001403, 2002b.

Topping, D. O., McFiggans, G. B., and Coe, H.: A curved multi-component aerosol hygroscopicity model framework: Part 2 – Including organic compounds, Atmos. Chem. Phys., 5, 1223-1242, 2005.

Vaattovaara, P., Huttunen, P. E., Yoon, Y. J., Joutsensaari, J., Lehtinen, K. E. J., O'Dowd, C. D., and Laaksonen, A.: The composition of nucleation and Aitken modes particles during coastal nucleation events: evidence for marine secondary organic contribution, Atmos. Chem. Phys., 6, 4601-4616, 2006.

Villani, P., Sellegri, K., Monier, M., and Laj, P.: Influence of semi-volatile species on particle hygroscopic growth, Atmos. Chem. Phys. Discuss., 9, 2021-2047, 2009.

Zardini, A. A., Sjogren, S., Marcolli, C., Krieger, U. K., Gysel, M., Weingartner, E., Baltensperger, U., and Peter, T.: A combined particle trap/HTDMA hygroscopicity study of mixed inorganic/organic aerosol particles, Atmos. Chem. Phys., 8, 5589-5601, 2008.

Zuend, A., Marcolli, C., Luo, B. P., and Peter, T.: A thermodynamic model of mixed organic-inorganic aerosols to predict activity coefficients, Atmos. Chem. Phys., 8, 4559-4593, 2008.

Chapter 5: Volcanic sulphate and arctic dust plumes over the North Atlantic Ocean

J. Ovadnevaite[1,2], D. Ceburnis[1], K. Plauskaite-Sukiene[2], **R. Modini**[3], R. Dupuy[1], I. Rimselyte[2], M. Ramonet[4], K. Kvietkus[2], Z. Ristovski[3], H. Berresheim[1], C. D. O’Dowd[1]

[1]School of Physics and Centre for Climate and Air Pollution Studies, Environmental Change Institute, National University of Ireland, Galway, Ireland

[2]Institute of Physics, Savanoriu 231, LT-02300 Vilnius, Lithuania

[3] International Laboratory for Air Quality and Health, Queensland University of Technology, Brisbane QLD 4000, Australia

[4]Laboratoire des Sciences du Climat et de l’Environment (LSCE), Gif sur Yvette, France

Atmospheric Environment, **43(32)**, 4968-4974, 2009

Statement of joint authorship

Title: Volcanic sulphate and arctic dust plumes over the North Atlantic Ocean

Authors: J. Ovadnevaite, D. Ceburnis, K. Plauskaite-Sukiene, R. Modini, R. Dupuy, I. Rimselyte, M. Ramonet, K. Kvietkus, Z. Ristovski, H. Berresheim, C. D. O'Dowd

J. Ovadnevaite

Developed concept; conducted field work and data analysis; wrote manuscript

D. Ceburnis

Developed concept; assisted with field work, interpretation of data and writing of the manuscript

K. Plauskaite-Sukiene

Conducted field work and assisted with SMPS data analysis

R. Modini

Conducted field work; analysed VH-TDMA data; wrote paragraphs of the manuscript related to the VH-TDMA (found in section on aerosol acidity); reviewed manuscript

R. Dupuy

Facilitated and processed SMPS data

I. Rimselyte

Assisted with data analysis

M. Ramonet

Facilitated and processed Radon data

K. Kvietkus

Assisted with data interpretation; reviewed manuscript

Z. Ristovski

Assisted with interpretation of VH-TDMA data; reviewed manuscript

H. Berresheim

Assisted with data interpretation and writing of manuscript

C. D. O’Dowd

Assisted with data interpretation; reviewed manuscript

Abstract

High time resolution aerosol mass spectrometry measurements were conducted during a field campaign at Mace Head Research Station, Ireland, in June 2007. Observations on one particular day of the campaign clearly indicated advection of aerosol from volcanoes and desert plains in Iceland which could be traced with NOAA Hysplit air mass back trajectories and satellite images. In conjunction with this event, elevated levels of sulphate and light absorbing particles were encountered at Mace Head. While sulphate concentration was continuously increasing, nitrate levels remained low indicating no significant contribution from anthropogenic pollutants. Sulphate concentration increased about 3.8 $\mu g/m^3$ in comparison with the background conditions. Corresponding sulphur flux from volcanic emissions was estimated to about 0.3 TgS/yr, suggesting that a large amount of sulphur released from Icelandic volcanoes may be distributed over distances larger than 1000 km. Overall, our results corroborate that transport of volcanogenic sulphate and dust particles can significantly change the chemical composition, size distribution, and optical properties of aerosol over the North Atlantic Ocean and should be considered accordingly by regional climate models.

Keywords: volcanic sulphate aerosol, Icelandic dust, particle acidity, aerosol properties

Introduction

Sulphuric acid and sulphate aerosols are essential precursors for cloud formation over the oceans (Charlson et al., 1987). They act as a cloud condensation nuclei and affect the number of cloud droplets increasing cloud albedo and may also lead to changes in precipitation (Textor et al., 2004). Nss-sulphate over the oceans can originate from both natural and anthropogenic sources and concentrations vary widely as a function of time and location (Savoie et al., 2002). Volcanic emissions of SO_4 and its sulphur precursor gases can significantly contribute to the natural SO_4 budget, even at the quiescent stage (Berresheim and Jaeschke, 1983; Glasow et al., 2008). According to Graf et al. (1997) the non-eruptive volcanic degassing of SO_2 and subsequent sulphate formation is estimated to be responsible for 24% of the global annual direct radiative forcing of sulphate aerosols. The annual SO_2 flux into the atmosphere from Icelandic volcanoes is about 0.8-1.0 Tg/yr (Halmer et al., 2002) thus representing one of the largest atmospheric sulphur sources in the North Atlantic region. These emissions may substantially contribute to new particle formation over this region and modify the composition of air masses, for example, of clean polar origin (O'Dowd and Smith, 1993).

Furthermore, Iceland has extensive arid regions, which are seldom reported in surveys, because the climatic environment and the composition of the sand make these deserts unusual. The sand originates largely from glacial margins, glacio-fluvial and volcanic deposits, and sedimentary rocks (Arnalds et al., 2001). Strong winds can generate dust storms over these deserts, and dust plumes may be transported over great distances impacting air quality in the British Isles and continental Europe (NASA, 2008; Prospero et al., 2008). Although dust storms may at times be relatively rare events, Prospero et al. (2008) pointed out that glaciers in Iceland have been retreating in recent decades and that this trend is expected to continue with changing climate. It is difficult to track the sulphate and dust plumes by composition analysis which is typically done with off-line techniques in long-term monitoring programmes such as Global Atmosphere Watch (GAW). Here we report real-time observations using a quadrupole aerosol mass spectrometer (Q-AMS) at the Mace Head Atmospheric GAW Research Station, on the west coast of Ireland, which enabled high time resolution measurements of size spectra and concentrations of organic and inorganic species in the sampled particles. Together with other real time measurement techniques operated at this station Q-AMS registered volcanic sulphate and Icelandic dust plumes in air advected over the North East Atlantic Ocean. Concurrent observations of aerosol size evolution and impact on light scattering are also discussed.

Experimental

A four-week field campaign was conducted in June 2007 at Mace Head Research Station, Ireland (53°19 ′ N, 9° 54 ′ W). The site has been described in detail by Jennings et al. (2003) and O'Connor et al. (2008). It is located on a peninsula and the wind direction sector between 190° and 300° is from the open North Atlantic Ocean providing excellent conditions for carrying out marine aerosol measurements.

All aerosol instruments were placed in the shore laboratory about 100 m from the coastline and 5 m above mean sea level, MSL. They were connected to the laminar flow community air sampling system, which is constructed from a 100 mm diameter stainless-steel pipe with the main inlet at 10 m above ground level.

The size resolved non-refractory chemical composition of submicron aerosol particles was measured with an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS, Aerodyne, Billerica, MA). The instrument is described by Jayne et al. (2000). Ionization efficiency was calibrated twice (at the very beginning and the end of the campaign) by 300 nm dry ammonium nitrate particles, according to the method described by Jimenez et al. (2003) and Allan et al. (2003). Measurements were performed with a time resolution of 5 min, with a vaporizer temperature of about 600 °C. A collection efficiency of CE = 0.5 was applied for the measurement period discussed here. According to laboratory experiments (Matthew et al., 2008, Middlebrook and Bahreini, 2008) the AMS collection efficiency depends on the particle chemical composition and relative humidity of the environment. They showed that at relative humidity about 80% and neutralization of sulphate particles about 50-60 %, which was the case during the analysed event, collection efficiency of AMS is about 0.5.

The total aerosol scattering coefficient and the hemispheric backscattering coefficient were measured with a TSI (TSI Incorporated, Shoreview, MN) Model 3563 three-wavelength (450; 550; 700 nm) integrating nephelometer.

Aerosol absorption measurements were performed with the Thermo scientific (Thermo Fisher Scientific Inc., Waltham, MA) multi-angle absorption photometer (MAAP) instrument, model 5012. This instrument calculates absorbance from particles deposited on a filter using measurements of both transmittance and reflectance at two different angles.

Aerosol size distributions were measured by a scanning mobility particle sizer (SMPS). The SMPS system is composed of a differential mobility analyzer (DMA, TSI model 3071), a condensation particle counter (CPC, TSI model 3010), an aerosol neutralizer (TSI 3077), a control unit, and a data logging system.

A volatility-hygroscopic-tandem differential mobility analyser (VH-TDMA) was employed to simultaneously measure the volatile and hygroscopic properties of particles ranging from 10 nm to 110 nm in (mobility) diameter (Johnson et al., 2004). Comparison of VH-TDMA signatures measured in the field with those of laboratory aerosols of known chemical composition were used to infer the composition of the atmospheric particles and their mixing state. A thorough description of the VH-TDMA and its operating procedures has been provided by Fletcher et al. (2007).

Radon (^{222}Rn) and lead (^{212}Pb) isotope concentrations were determined using the active deposit method. The absolute error is estimated to be in the order of 20% (Polian et al., 1986; Biraud et al., 2000).

Backward trajectories up to 96 hours were calculated, using the National Oceanic and Atmospheric Administration (NOAA) hybrid single-particle lagrangian integrated trajectory (HY-SPLIT) model ((Draxler and Hess, 1997). Trajectories were calculated for every hour at three different altitudes: 1000, 500 and 20 meters above ground level (AGL).

Results

On June 26, 2007, a high pressure system over Greenland and a low situated over the North Atlantic Ocean and Ireland produced a north westerly flow with 8 m/s average local wind speed and quite low temperature – about 12-14 ºC during the day. The relative humidity varied between 80% and 90 % and particle concentration was less than 700 particles cm^{-3}, typical for marine background air at Mace Head. Local wind direction shifted from 360º to 270º and between 11:00 UTC and 24:00 UTC it was from the typical marine sector (which extends between 190º and 300º). The air mass trajectories gradually shifted from north to west, and from 04:00 UTC had passed over Iceland approximately three days earlier before reaching Mace Head (Fig. 5.1).

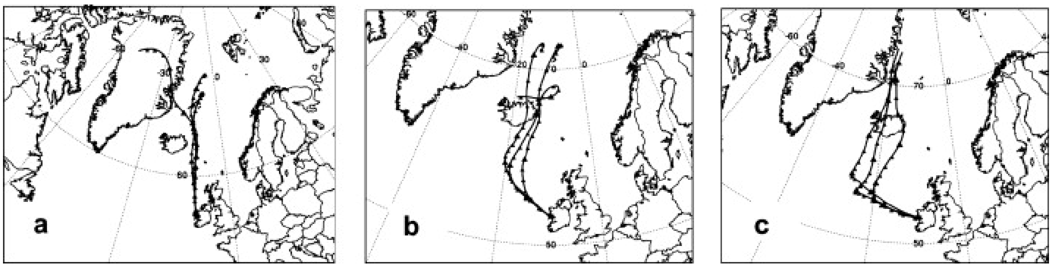


Figure 5.1: Evolution of air mass back trajectories, calculated for June 26, 2007 (NOAA HYSPLIT): a) 02:00 UTC; b) 11:00 UTC; c) 19:00 UTC. Backward trajectories length was up to 96 hours at three different altitudes: 1000, 500 and 20 meters above ground level.

Evolution of the aerosol composition

We observed a continuous increase in sulphate concentrations in advected air masses with trajectories crossing over Iceland. Over the period of 11 hours the non-sea salt (nss)-sulphate concentration increased from 1.2 to 4.6 (±0.9) µg/m^3 (Fig. 5.2). Concurrent nitrate levels remained low and largely unchanged indicating no major contribution from anthropogenic pollution.

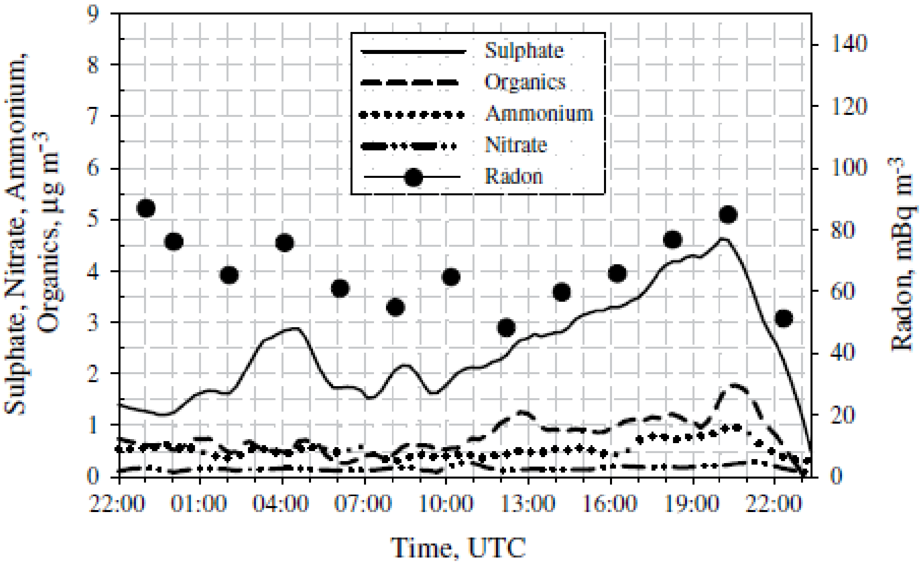


Figure 5.2: Temporal trends of chemical composition of PM1 aerosol, measured by Q-AMS and concurrent radon concentrations on June 26, 2007.

A minor increase was observed in the level of organics, probably originating from phytoplankton blooms located south-west of Iceland (NASA, 2008). However, the lack of correlation (R^2=0.02) between organic and sulphate trends suggests that the observed increase in sulphate concentration was associated with a different source. Moreover, marine biogenic nss-sulphate concentrations at Mace Head station as reported by Yoon et al. (2007) are less than 0.8 µg/m^3. In addition, the concurrent increase in radon concentrations (Fig. 5.2) supports a predominantly land origin of sulphate in this air mass. Radon concentrations were initially elevated due to regional contributions from Ireland but then decreased when trajectories shifted from north to north-west. Later (from 12:00

UTC) it started increasing again in conjunction with air mass passage over Iceland. The radon temporal trend followed the sulphate trend. Generally, the radon concentration on June 26 was lower than 400 mBq/m^3 indicating an oceanic air mass (Messager et al., 2008) and little to no contact with land over the past 2-3 days. This is consistent with the measurements of ^{212}Pb as lead concentration decreased after 12:00 UTC and stayed at low level until the end of the day. ^{222}Rn and ^{212}Pb are both emitted by soils and can be used as continental tracers. However, they have different radioactive decay time: 3.8 days for ^{222}Rn and 10.6 hours for ^{212}Pb. Therefore, a decrease in concentration of the latter tracer showed the absence of a recent contact with land, whereas increase in the radon concentration indicated a remote land influence.

From these results we assume that the observed increase in sulphate concentration (3.4 μg/m^3 above background level) was entirely caused by advection of volcanic sulphur emissions from Iceland. Using the time period of 11 hours and the 3.4 μg/m^3 increase in nss-sulphate levels we estimated the total sulphur flux from Icelandic volcanoes assuming that all SO_2 had been converted to sulphate. The measured increase in concentration was multiplied by the total volume of the plume which could be derived using the FLEXPART model (Stohl et al., 2005). The mixed layer height was assumed to be 1 km. We calculated a sulphur flux of 820 t S/d. Assuming constant emissions this result was scaled to the yearly sulphur flux to compare it with previous estimates of annual fluxes of sulphur from Icelandic volcanoes and from dimethylsulphide (DMS) emissions from the North Atlantic.

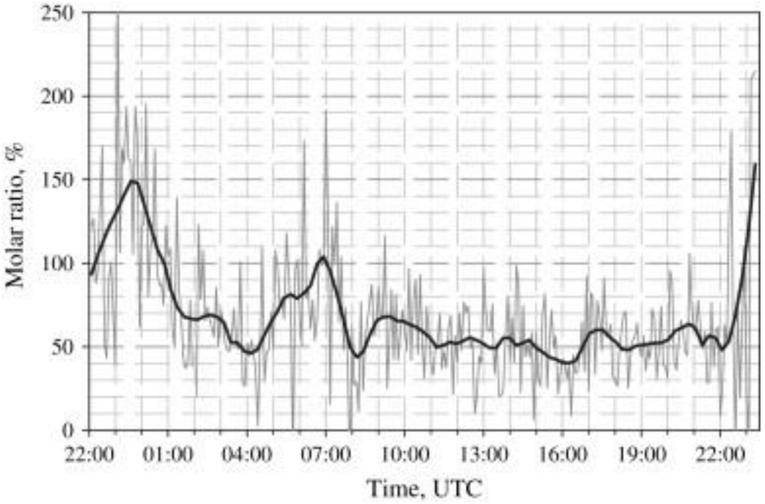


Figure 5.3: Time trends of ammonium to sulphate molar ratios in PM1 aerosol, measured by Q-AMS on June 26, 2007. There are 2 mol of ammonium for every mole of sulphate consequently when sulphate is fully neutralized in the form of ammonium sulphate the ratio is 200%, when sulphate is ammonium bisulphate ratio is 100%, and for particulate sulphuric acid ratio is 0.

Volcanic aerosol acidity

The sulphate particles were only partially neutralized by ammonium based on the results obtained by both the Q-AMS and the Volatility Hygroscopic Tandem Differential Mobility Analyzer (VH-TDMA). Q-AMS measured at least 35% of the total sulphate mass being a pure sulphuric acid (Fig. 5.3) while according to VH-TDMA, H_2SO_4 constituted about 26% of total sulphate volume in 50nm particles.

The modified marine air flow touching the west coast of Ireland (Fig. 5.1a) in conjunction with northerly wind direction brought nearly neutralized sulphate particles in the form of ammonium sulphate and bisulphate (00:00 UTC - 01:00 UTC, Fig. 5.3). However, with trajectories shifting to the west and air masses coming from the marine sector (Fig. 5.1b, c), the degree of neutralization decreased and sulphuric acid constituted about 50 % of the total sulphate mass (10:00 UTC- 23:00 UTC, Fig. 5.3).

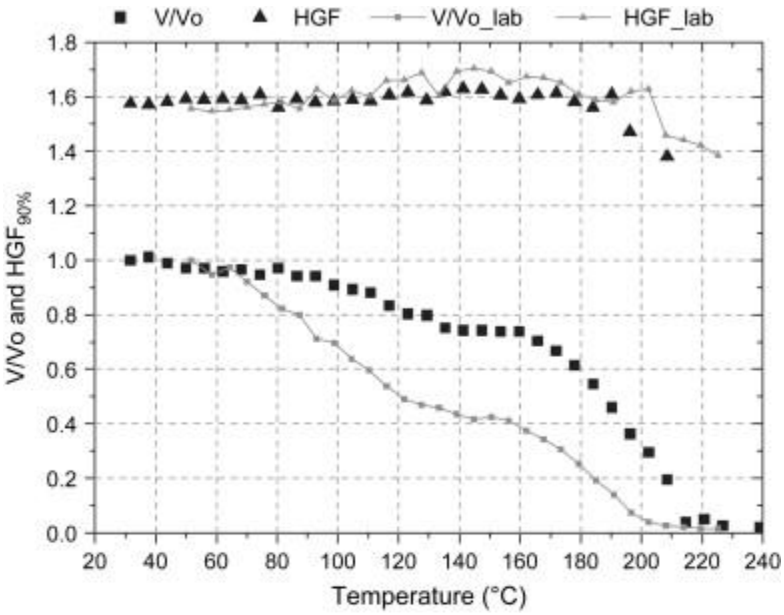


Figure 5.4: VH-TDMA scan of 50 nm particles completed between 13:55 UTC and 15:26 UTC on June 26. Volume fraction remaining (V/Vo) and Hygroscopic Growth Factor (HGF) at 90% RH are both displayed as a function of thermodenuder temperature. Also plotted are the corresponding curves for 100 nm partially neutralized H_2SO_4 particles measured in the laboratory by Johnson et al. (2005). The two steps in the laboratory measured volatility curve correspond to evaporation of H_2SO_4 (60–150 °C) and ammoniated sulphate (160–220 °C).

Figure 5.4 displays a VH-TDMA scan of 50 nm particles completed between 13:55 UTC and 15:26 UTC on June 26. The volatility curve (particle volume fraction remaining (V/Vo) against thermodenuder temperature) had 2 distinct volatilisation steps. The first component evaporated at 80-140ºC and the second component evaporated at 160-220ºC. Comparison with a VH-TDMA scan of laboratory generated, partially neutralised sulphuric acid (H_2SO_4) particles (Johnson et al. 2005) suggests that the more volatile component is H_2SO_4 and the less volatile component is partially neutralised H_2SO_4 (ammoniated sulphate). For the ambient scan the volume fraction of H_2SO_4 is 26%. A repeat scan conducted between 16:15 UTC and 16:53 UTC was very similar to the original scan. The volume fraction of H_2SO_4 was, again, 26%.

The degree of neutralisation was calculated assuming that any ammoniated sulphate existed as letovicite ($(NH_4)_3H(SO_4)_2$). This assumption is based on the measured fraction of sulphuric acid and the H_2O-$(NH_4)_2SO_4$-H_2SO_4 phase diagram presented by Tang et al. (1978). The per-particle volumes of H_2SO_4 and $(NH_4)_3H(SO_4)_2$ were calculated from the initial particle diameters and particle diameters at 150ºC and 220ºC. These volumes were converted to mole numbers using density and molecular weight. The density of H_2SO_4 was calculated according to the parameterisation of Tang (1996). Finally, considering the stoichiometry of letovicite the ammonium to sulphate ratio was calculated to be 110.5%.

However, with respect to particle size the Q-AMS covered the 40-1000 nm diameter range of particles, whereas VH-TDMA measured the composition of only 50 nm particles at that time. Therefore the combined results suggest that there was a greater degree of neutralisation for smaller particles. Previous studies e.g., by Fletcher et al. (2007) at Cape Grim station and Tomlinson et al. (2007) over the south-eastern Pacific also reported a relatively stronger neutralization in lower particle sizes. They suggested that size dependent acidity could be explained by H_2SO_4 being added to the aerosol by in-cloud aqueous phase processes faster than it can be neutralized by the limited available ammonium. On the other hand, smaller particles may simply be neutralized by the limited ammonium more readily due to their higher surface-volume ratio (McMurry et al. 1983). In our study both instruments showed the presence of pure sulphuric acid in the particles which is consistent with previous study of Satsumabayashi et al. (2004) who showed that aerosols affected by volcanic emissions were strongly acidic as the excess amount of SO_4^{2-} exhausted ammonium and partially expelled NO_3^- and Cl^-. Furthermore, Stothers and Rampino (1983) demonstrated that the largest acidity signals in old Greenland ice are due to European (Mediterranean and Icelandic) volcanic eruptions. Typically, the ammonium to sulphate ratio measured near a volcanic source is much lower compared to a site further downwind (Johnson and Parnell, 1986; Mather et al., 2003).

Aerosol radiative absorption and scattering

In addition to sulphate plume, an increase in absorption was registered by multi-angle absorption photometer (MAAP). Figure 5.6 shows that noticeable amount of absorbing material was measured between 16:15 UTC and 20:30 UTC. The Moderate Resolution Imaging Spectroradiometer (MODIS) flying on NASA's Terra satellite captured the image of dust plumes blowing off the southern coast of Iceland over the North Atlantic Ocean on June 23, 2007 (Fig. 5.5). Thus following this event, elevated concentrations of light absorbing particles were encountered at Mace Head (Fig. 5.6).

Figure 5.5: Dust storm blowing off the southern coast of Iceland over the North Atlantic Ocean on June 23, 2007 (NASA, 2008).

MAAP is a filter-based technique for measuring aerosol light absorption; it relies on the change in transmission of light through a filter as it is loaded with aerosol to determine the aerosol absorption coefficient. Similarly to other filter-based techniques measurements can be biased during specific conditions (Lack et al., 2008) such as high loadings of dust aerosol. Dust particles can both absorb and scatter sunlight (Miller et al., 2004). Consistent with these properties our measurements showed a good correlation between light absorption and both back and total (back plus forward) scattering coefficients (Fig. 5.6). Several previous studies demonstrated that dust events increased scattering coefficients and nephelometer could be used as a good indicator of dust particle advection (Ichoku C. et al. 1999; Kim et al., 2004; Derimian et al., 2006). During advection of Icelandic dust to Mace Head , the total scattering coefficient followed similar trends at all three wavelengths (450, 550, 700 nm) whereas the backscattering coefficient was more spread between different wavelengths of light although they showed a similar time trend. These differences between wavelengths became significant (~15-20%) when the fraction of the organic aerosol material increased (12:00-13:00 UTC, 20:00-21:00 UTC) showing an inhomogeneous particle size distribution. In addition, Figure 5.6 shows that the light-scattering associated by sulphate aerosol was lower compared to the dust particles. Aerosol light scattering coefficients peaked at the same time as absorption maximum and only qualitatively followed sulphate concentration increase.

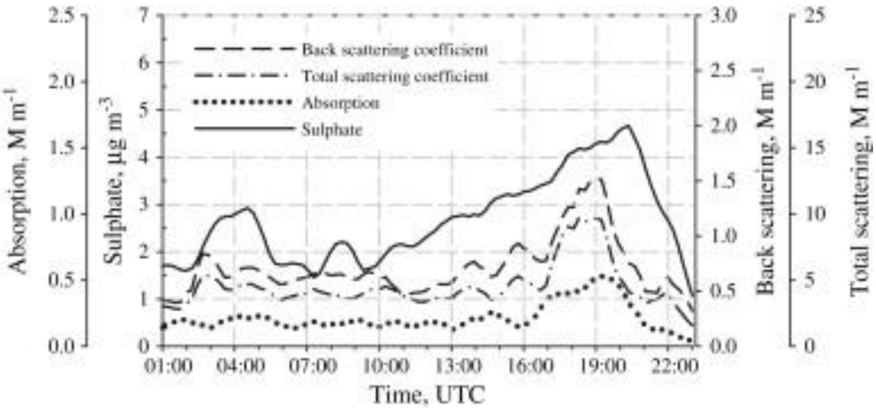


Figure 5.6: Enhancement of scattering coefficients and absorption due to increase in sulphate concentration and dust particles levels on June 26, 2007.

Aerosol size distribution

During the studied event, the aerosol size distribution was bimodal with well defined Aitken and accumulation modes. Figure 5.7 presents the temporal evolution of the aerosol size spectrum. Initially, a higher fraction of sulphate resulted in the growth of both accumulation and Aitken mode particles. However, this changed later due to the increasing fraction of dust particles. Consequently from 16:30 UTC we observed both higher absorption levels and a concurrent change in the size distribution (17:30 UTC). The Aitken mode diameter continued to increase while the accumulation mode diameter shifted towards smaller sizes (Table 5.1). In addition, dust particles increased the number concentration in both the Aitken and accumulation modes.

From 20:30 UTC air masses were advected from the North Atlantic Ocean which had not passed over Iceland. In this context, a rapid decrease in sulphate concentrations and significant change in the aerosol size spectrum was observed resulting in typical aerosol size distribution for a very clean air mass at Mace Head (Yoon et al., 2007).

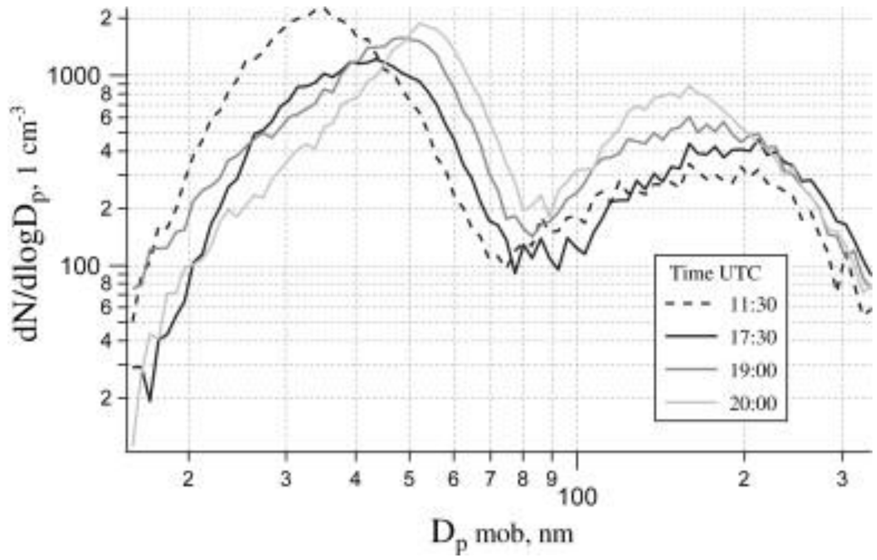


Figure 5.7: Evolution of bimodal size distribution, measured by SMPS on June 26, 2007.

Table 5.1: Summary of the modal parameters obtained by fitting lognormal functions to aerosol number size distribution measured by SMPS in Mace Head on June 26.

Time, UTC	11:30	14:00	15:50	17:30	19:00	20:00	21:30
Aitken mode median diameter, nm	34±0.1	34±0.1	35±0.1	41±0.2	46±0.3	52±0.3	36±0.2
Number concentration, cm^{-3}	613±11	471±9	439±9	383±7	473±8	437±9	218±3
Accumulation mode median diameter, nm	162±4	184±3	191±4	186±2	163±4	154±2	209±4
Number concentration, cm^{-3}	130±1	127±2	129±2	158±2	209±2	263±4	108±1

Discussion

In general, the climate relevant implications of volcanic eruptions have been recognized in previous studies (Toon and Pollack, 1980; Gilliland, 1982; Rampino and Self, 1984; Minnis et al., 1993; Robock A., 2000). However, quasi-continuous non-eruptive emissions may have an even stronger incremental climatic impact than the relatively brief cataclysmic eruptions (Graf et al., 1997). For example, the annual sulphur input into the atmosphere from Icelandic volcanoes is of the same range as the total sulphur flux from the dimethylsulphide over the whole North Atlantic Ocean, 0.5 TgS/yr (Halmer et al., 2002) and 1.3 TgS/yr (Kettle and Andreae, 2000) respectively. Moreover, we estimated that Icelandic volcanogenic sulphur flux was about 0.3 TgS/yr (see previous section for details) suggesting that a large amount of sulphur emissions from Icelandic volcanoes can reach distances larger than 1000 km (Iceland to Ireland distance is approximately 1300 km). Such calculations, based on one event, should be considered as a rough estimate of the regional impact of degassing sulphur emissions; however they are in a good agreement with the previous calculations of total sulphur flux from Icelandic volcanoes (Halmer et al., 2002). Thus despite its relative point source character the distribution of sulphur from Icelandic volcanoes over the North Atlantic region was comparable to the larger scale input from marine biogenic sources.

The most obvious and well known volcanic effect is on solar radiation, since the sulphate particles are about the same size as the visible light wavelength (Robock, 2000). Though only a relatively small fraction of sulphate is directly emitted from volcanoes, the bulk of the sulphate aerosol is formed during the long range transport of the emissions by both gas and aqueous phase oxidation of SO_2 (Hegg, 1985), affecting the resulting aerosol size distribution. Our observations of a typical aerosol bimodal size distribution during the volcanic plume event suggest a significant cloud processing of the aerosol along the trajectory path where accumulation mode was formed by cloud activation of Aitken mode particles (Hoppel et al., 1986; Fitzgerald, 1991; Bott, 1999; O'Dowd et al., 2000).

Presumably two processes took place during this transport: a new sulphate aerosol formation and its subsequent neutralization by cations such as ammonium. As measurements near volcanoes show highly acidic aerosol (Johnson and Parnell, 1986; Mather et al., 2003; Satsumabayashi et al., 2004), the partially neutralised aerosol measured at Mace Head indicates the chemical aerosol evolution during air mass transport. Along with the chemical transformation the physical aerosol properties have been changing as well, with the increasing fraction of sulphate resulting in the growth of both accumulation and Aitken mode particles. Moreover, concurrent advection of dust particles from Icelandic deserts contributed to further modifications of the aerosol properties. Dust particles were identified by two independent albeit indirect measurements using the three-wavelength integrating nephelometer and the multi-angle absorption photometer. We observed a corresponding increase by about 60% in light absorption and scattering caused by advected sulphate and dust particles which indicates their strong climatic implications.

Conclusion

Advection of volcanogenic sulphate aerosol from Iceland significantly increased sulphate concentrations at Mace Head. Moreover it was shown that the corresponding volcanic plume caused a substantial modification in the aerosol chemical composition and size distribution over the North Atlantic region during transport. Over the period of 11 hours the non-sea salt sulphate concentration increased by a factor of four while concurrent nitrate and organic levels remained low and largely unchanged. The sulphate particles were only partially neutralized. The Q-AMS measurements showed that at least 35% of the total sulphate mass was pure sulphuric acid in submicrometer (PM1) aerosol. Concurrent VH-TDMA measurements showed that H_2SO_4 constituted about 26% of the total sulphate volume in particles of 50 nm diameter size. The combined results suggest that there was a relatively larger degree of neutralisation by ammonium in smaller particles. The predominant fraction of sulphate aerosol is assumed to have been formed by aqueous phase oxidation of SO_2 based on the efficiency of this process and the cloud cover associated with the air mass trajectories. A concurrent dust outbreak from Iceland increased the levels of absorbing material and the light-scattering. Aerosol light scattering coefficients peaked at the same time as absorption maximum and qualitatively followed sulphate concentration increase. Evaluated sulphur flux demonstrated that a large amount of the total (non-eruptive) sulphur emissions from Icelandic volcanoes can reach distances larger than 1000 km. These results in conjunction with previous research suggest that volcanogenic emissions and Aeolian dust from Arctic deserts in Iceland can be potentially significant regional sources of aerosols over the North Atlantic and therefore should be adequately considered in regional and global climate models.

Acknowledgements

This work was supported by the EU projects ACCENT (subproject Access to research infrastructures), EUSAAR TNA, SFI (Science Foundation Ireland, grant 08/RFP/GEO1233), EPA Ireland and ESF (European Science Foundation, activity: INTROP). Authors wish to thank anonymous reviewers for their constructive and helpful comments.

References

Allan J.D., Jimenez J.L., Williams P.I., Alfarra M.R., Bower K.N., Jayne J.T., Coe H., Worsnop D.R., 2003. Quantitative sampling using an Aerodyne aerosol mass spectrometer 1. Techniques of data interpretation and error analysis. Journal of Geophysical Research 108 (D3), 4090–4100.

Arnalds O., Gisladottir F. O., Sigurjonsson H., 2001. Sandy deserts of Iceland: an overview. Journal of Arid Environments 47, 359–371

Berresheim H., Jaeschke W., 1983. The contribution of volcanoes to the global atmospheric sulfur budget, Journal of Geophysical Research 88, 3732-3740.

Biraud S., Ciais P., Ramonet M., Simmonds P., Kazan V., Monfray P., O'Doherty S., Spain T. G., Jennings S. G., 2000. European greenhouse gas emissions estimated from continuous atmospheric measurements and radon 222 at Mace Head, Ireland. Journal of Geophysical Research 105(D1), 1351–1366.

Bott A., 1999. A numerical model of the cloud-topped planetary boundary-layer: cloud processing of aerosol particles in marine stratus. Environmental Modelling and Software 14, 635-643.

Charlson R. J., Lovelock J. E., Andreae M. O., Warren S. G., 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature 326, 655–661.

Derimian Y., Karnieli A., Kaufman Y. J., Andreae M. O., Andreae T. W., O. Dubovik, W. Maenhaut, I. Koren, and B. N. Holben, 2006. Dust and pollution aerosols over the Negev desert, Israel: Properties, transport, and radiative effect, Journal of Geophysical Research 111, D05205, doi:10.1029/2005JD006549.

Draxler R.R., Hess G.D., 1997. Description of the Hysplit_4 modeling system. NOAA Tech Memo ERL ARL-224, 24p. (http://www.arl.noaa.gov/ready/hysplit4.html)

Fitzgerald J.W., 1991. Marine aerosols: A review. Atmospheric Environment - Part A General Topics 25, Issue 3-4, 533-545.

Fletcher C. A., Johnson G. R., Ristovski Z. D., Harvey, M., 2007. Hygroscopic and volatile properties of marine aerosol observed at Cape Grim during the P2P campaign. Environmental Chemistry 4, 162-171.

Gilliland, R. L., 1982. Solar, volcanic, and CO2 forcing of recent climatic changes, Climatic Change 4, 111–131.

Glasow R., Bobrowski N., Kern C., 2008. The effects of volcanic eruptions on atmospheric chemistry. Chemical Geology, Article in Press.

Graf H.-F., Feichter J. , Langmann B., 1997. Volcanic sulfur emissions: Estimates of source strength and its contribution to the global sulfate distribution, Journal of Geophysical Research 102(D9), 10,727–10,738.

Halmer M.M., Schmincke H.U., Graf H.F., 2002. The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years. Journal of Volcanology and Geothermal Research 115, 511-528.

Hegg D.A., 1985. The importance of liquid phase oxidation of SO2 in the troposphere. Journal of Geophysical Research 90, 3773-3779.

Hoppel W. A., Frick G. M., Larson R. E., 1986. Effect of nonprecipitating clouds on the aerosol size distribution in the marine boundary layer, Geophysical Research Letters 13, 125–128.

Ichoku C., Andreae M.O., Andreae T.W., Meixner F.X., Schebeske G., Formenti P., Maenhaut W., Cafmeyer, J., Ptasinski, J., Karnieli, A., Orlovsky L., 1999. Interrelationships between aerosol characteristics and light scattering during late winter in an Eastern Mediterranean arid environment, Journal of Geophysical Research 104(D20), 24,371–24,393.

Jayne J.T., Leard D.C., Ahang X., Davidovits P., Smith K.A., Kolb C.E., Worsnop D.R., 2000. Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. Aerosol Science and Technology 33 (1–2), 49–70.

Jennings S. G., Kleefeld C., O’Dowd, Junker C., Spain T. G., O’Brien P., Roddy A. F., O’Connor T. C., 2003. Mace Head atmospheric research station—Characterization of aerosol radiative parameters. Boreal Environment Research 8, 303 – 314.

Jimenez J.L., Jayne J.T., Shi Q., Kolb C.E., Worsnop D.R., Yourshaw I., Seinfeld J.H., Flagan R.C., Zhang X., Smith K.A., Morris J.W., Davidovits P., 2003. Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer. Journal of Geophysical Research 108 (D7), 8245–8258.

Johnson N. and Parnell R. A., 1986. Composition, distribution and neutralization of ‘acid rain’ derived from Masaya volcano, Nicaragua. Tellus 38B, 106–117.

Johnson G. R., Ristovski Z., Morawska L., 2004. Method for measuring the hygroscopic behaviour of lower volatiliy fractions in an internally mixed aerosol. Journal of Aerosol Science 35, 443-455.

Johnson G. R., Ristovski Z. D., D'Anna B., Morawska L., 2005. Hygroscopic behaviour of partially volatilised coastal marine aerosols using the volatilisation and humidification tandem differential mobility analyser technique. Journal of Geophysical Research 110, D20203.

Kettle A. J., Andreae M. O., 2000. Flux of dimethylsulfide from the oceans: A comparison of updated data sets and flux models, Journal of Geophysical Research 105, 26,793–26,808.

Kim K. W., He Z., Kim Y. J., 2004. Physicochemical characteristics and radiative properties of Asian dust particles observed at Kwangju, Korea, during the 2001 ACE-Asia intensive observation period, Journal of Geophysical Research 109, D19S02, doi:10.1029/2003JD003693.

Lack D., Cappa C., Covert D., Baynard T., Massoli P., Sierau B., Bates T., Quinn P., Lovejoy E., Ravishankara A. R. Bias in Filter-Based Aerosol Light Absorption Measurements Due to Organic Aerosol Loading: Evidence from Ambient Measurements (2008) Aerosol Science and Technology, 42:1033–1041.

Mather T. A., Allen A. G., Oppenheimer C., Pyle D. M., McGonigle A. J. S., 2003. Size-Resolved Characterisation of Soluble Ions in the Particles in the Tropospheric Plume of Masaya Volcano, Nicaragua: Origins and Plume Processing. Journal of Atmospheric Chemistry 46, 207–237.

Matthew B.M., Middlebrook A.M., Onasch T.B., 2008. Collection Efficiencies in an Aerodyne Aerosol Mass Spectrometer as a Function of Particle Phase for Laboratory Generated Aerosols. Aerosol Science and Technology 42(11), 884-898, DOI: 10.1080/02786820802356797

McMurry P. H., Takano H., Anderson G. R., 1983. Study of the Ammonia (Gas)- Sulphuric Acid (Aerosol) Reaction Rate. Environmental Science and Technology 17, 347-352.

Messager C., Schmidt M., Ramonet M., Bousquet P., Simmonds P., Manning A., Kazan V., Spain G., Jennings S. G., Ciais P., 2008. Ten years of CO2, CH4, CO and N2O fluxes over Western Europe inferred from atmospheric measurements at Mace Head, Ireland. Atmospheric Chemistry and Physics Discussions 8, 1191–1237.

Middlebrook A. Bahreini R., 2008. Applying Laboratory Collection Efficiencies to Ambient Field Data. AMS Users' Meeting 2008. Accessed on 18.02.2009

http://cires.colorado.edu/jimenez-group/UsrMtgs/UsersMtg9/09_Middlebrook_CE.pdf

Miller R.L., Tegen I., Perlwitz J., 2004. Surface radiative forcing by soil dust aerosols and the hydrologic cycle. Journal of Geophysical Research 109 (D4), D04203.

Minnis, P., E. F. Harrison, L. L. Stowe, G. G. Gison, F. M. Denn, D. R. Doelling, and W. L. Smith Jr., 1993. Radiative climate forcing by the Mount Pinatubo eruption, Science259, 1411–1415.

NASA (2008). Accessed on 11/05/2009.

http://earthobservatory.nasa.gov/NaturalHazards/view.php?id=18595&oldid=14345.

O'Connor T.C., Jennings S.G., O'Dowd C.D., 2008. Highlights of fifty years of atmospheric aerosol research at Mace Head, Atmospheric Research 90, 338-355.

O'Dowd C.D., Smith M.H., 1993./ Physicochemical properties of aerosols over the northeast Atlantic: evidence for wind-speed-related submicron sea-salt aerosol production. Journal of Geophysical Research 98 (D1), 1137-1149.

O'Dowd C. D., Low, J. A., Smith M. H., 2000. The effect of clouds on aerosol growth in the rural atmosphere. Atmospheric Research 54, 4, 201-221.

Polian G., Lambert G., Ardouin B., and Jegou A., 1986. Long-range transport of continental radon in subantarctic and antarctic areas, Tellus 38B, 178–189.

Prospero J. M., Arnalds Ó., Olafsson H., Bullard J. E., Hodgkins R., 2008. Iceland Dust Storms Linked to Glacial Outwash Deposits and to Sub-Glacial Flood (Jökulhlaup) Events, Eos Trans. AGU 89 (53), Fall Meeting Supplementary, Abstract A13E-08

Rampino, M. R., and S. Self, 1984. Sulphur-rich volcanic eruptions and stratospheric aerosols, Nature, 310, 677–679.

Robock A., 2000. Volcanic eruptions and climate. Reviews of Geophysics 38, 191–219.

Satsumabayashi H., Kawamura M., Katsuno T., Futaki K., Murano K., Carmichael G. R., Kajino M., Horiguchi M., Ueda H., 2004. Effects of Miyake volcanic effluents on airborne particles and precipitation in central Japan, Journal of Geophysical Research 109, D19202.

Savoie D. L., Arimoto R., Keene W. C., Prospero J. M., Duce R. A., Galloway J. N., 2002. Marine biogenic and anthropogenic contributions to non-sea-salt sulfate in the marine boundary layer over the North Atlantic Ocean, Journal of Geophysical Research 107(D18), 4356

Stohl A., Forster C., Frank A., Seibert P. and Wotawa G., 2005. Technical Note: The Lagrangian particle dispersion model FLEXPART version 6.2. Atmospheric Chemistry and Physics 5, 2461-2474. http://niflheim.nilu.no/~burkhart/EUCAARI/MHD/MHD_200706/

Stothers r. B., Rampino M. R., 1983. Historic Volcanism, European Dry Fogs, and Greenland Acid Precipitation, 1500 B.C. to A.D. 1500. Science, New Series, Vol. 222, 4622, 411-413.

Tang I. N., Munkelwitz H. R., Davis J. G., 1978. Aerosol Growth Studies- IV. Phase Transformation of Mixed Salt Aerosols in a Moist Atmosphere. Journal of Aerosol Science 9, 505-511.

Tang I. N., 1996. Chemical and size effects of hygroscopic aerosols on light scattering coefficients. Journal of Geophysical Research 101, 19,245–19,250.

Textor C., Graf H. F., Timmreck C., and Robock A., 2004. Emissions from volcanoes. In Emissions of Atmospheric Trace Compounds, Claire Granier, Paulo Artaxo, and Claire Reeves, Eds., (Kluwer, Dordrecht), 269-303.

Tomlinson J. M., Li R., Collins D. R., 2007. Physical and chemical properties of the aerosol within the southeastern Pacific marine boundary layer. Journal of Geophysical Research 112, D12211, doi:10.1029/2006JD007771.

Toon, O. B., and Pollack J. B., 1980. Atmospheric aerosols and climate, American Scientist 68, 268–278.

Yoon Y. J., Ceburnis D., Cavalli F., Jourdan O., Putaud J. P., Facchini M. C., Decesari S., Fuzzi S., Jennings S. G., O'Dowd C. D., 2007. Seasonal characteristics of the physico-chemical properties of North Atlantic marine atmospheric aerosols. Journal of Geophysical Research 112, D04206; doi: 10.1029/2005JD007044.

Chapter 6: The organic fraction of bubble-generated, accumulation mode Sea Spray Aerosol (SSA)

R. L. Modini[1], B. Harris[1], Z. D. Ristovski[1]

[1] International Laboratory for Air Quality and Health, Queensland University of Technology,
Brisbane QLD 4000, Australia

Atmospheric Chemistry and Physics, **10(6)**, 2867-2877, 2010

Statement of joint authorship

Title: The organic fraction of bubble-generated, accumulation mode Sea Spray Aerosol (SSA)

Authors: R. L. Modini, B. Harris, Z. D. Ristovski

R. L. Modini

Developed concept, experimental design and scientific method; conducted field work; analysed and interpreted the data; wrote manuscript

B. Harris

Conducted field work

Z. D. Ristovski

Contributed to concept, experimental design and scientific method; reviewed manuscript

Abstract

Recent studies have detected a dominant accumulation mode (~100 nm) in the Sea Spray Aerosol (SSA) number distribution. There is evidence to suggest that particles in this mode are composed primarily of organics. To investigate this hypothesis we conducted experiments on NaCl, artificial SSA and natural SSA particles with a Volatility-Hygroscopicity-Tandem-Differential-Mobility-Analyser (VH-TDMA). NaCl particles were atomiser generated and a bubble generator was constructed to produce artificial and natural SSA particles. Natural seawater samples for use in the bubble generator were collected from biologically active, terrestrially-affected coastal water in Moreton Bay, Australia. Differences in the VH-TDMA-measured volatility curves of artificial and natural SSA particles were used to investigate and quantify the organic fraction of natural SSA particles. Hygroscopic Growth Factor (*HGF*) data, also obtained by the VH-TDMA, were used to confirm the conclusions drawn from the volatility data. Both datasets indicated that the organic fraction of our natural SSA particles evaporated in the VH-TDMA over the temperature range 170–200°C. The organic volume fraction for 71–77 nm natural SSA particles was 8±6%. Organic volume fraction did not vary significantly with varying water residence time (40 secs to 24 hrs) in the bubble generator or SSA particle diameter in the range 38–173 nm. At room temperature we measured shape- and Kelvin-corrected *HGF* at 90% RH of 2.46±0.02 for NaCl, 2.35±0.02 for artifical SSA and 2.26±0.02 for natural SSA particles. Overall, these results suggest that the natural accumulation mode SSA particles produced in these experiments contained only a minor organic fraction, which had little effect on hygroscopic growth. Our measurement of 8±6% is an order of magnitude below two previous measurements of the organic fraction in SSA particles of comparable sizes. We stress that our results were obtained using coastal seawater and they can’t necessarily be applied on a regional or global ocean scale. Nevertheless, considering the order of magnitude discrepancy between this and previous studies, further research with independent measurement techniques and a variety of different seawaters is required to better quantify how much organic material is present in accumulation mode SSA.

Introduction

Sea Spray Aerosol (SSA) is generated when air bubbles rise to the ocean surface and burst or when seawater droplets are torn from the crests of waves. These seemingly simple processes create the largest mass emission flux to the atmosphere of all aerosol types (Andreae and Rosenfeld, 2008). SSA particles vary in size over 5 decades from tens of nanometres to hundreds of micrometres. Large super-micrometre SSA particles account for the majority of sea spray mass in the atmosphere (>95%). However it is the sub-micrometre SSA particles that are by far the most numerous. In particular recent laboratory and field measurements have consistently detected a dominant mode in the SSA number distribution centred at ~100 nm dry diameter (Clarke et al., 2006; Martensson et al., 2003; O'Dowd and Smith, 1993; Sellegri et al., 2006; Tyree et al., 2007). In this study we will refer to this dominant mode as the SSA accumulation mode even though it extends to particle sizes traditionally placed in the Aitken mode (20–100 nm). The SSA accumulation mode is climatically very important because it means SSA can potentially account for a significant proportion of cloud condensation nuclei (CCN) in the remote marine environment, particularly under high wind conditions (Clarke et al., 2006; O'Dowd et al., 1997; Pierce and Adams, 2006).

Bursting bubbles produce SSA in the form of film drops and jet drops. The SSA accumulation mode most likely originates from film drops. These are generated when fragments of bubble film (cap) are ejected into the air as a bubble bursts. Secondary droplets created when some of these fragments collide with the air-water surface may also contribute to the SSA accumulation mode (Spiel, 1998). Milliseconds after a bubble burst (Spiel, 1995) jet drops are generated from the break-up of the upward moving jet column caused by the collapse of the bubble cavity. Jet drops are in the super-micrometre size range: they are roughly one tenth the size of their parent bubbles (Blanchard, 1989).

The composition of SSA is surprisingly complex. Seawater contains a range of inorganic salts which all exist in SSA. In addition SSA contains an organic fraction which is derived from on or near the ocean surface. The existence of an organic fraction in SSA was detected many years ago (Blanchard, 1964). A number of studies found that the concentration of organic carbon (Gershey, 1983; Hoffman and Duce, 1976) and bacteria (e.g. see Blanchard, 1989 and references therein) in bulk SSA is enriched hundreds of time relative to corresponding concentrations in source water. Enrichment of organic matter in SSA occurs because it is generated from bubbles bursting in an enriched layer of chemical and biological material on seawater surfaces known as the sea-surface micro-layer (e.g. Liss and Duce, 1997). Organic material, and in particular surface-active organic material, becomes concentrated at the sea-surface micro-layer by factors of up to 10 compared to sub-surface waters (Hunter, 1997) due to processes such as diffusion, turbulent mixing and scavenging and transport by rising air bubbles.

Decades ago it was hypothesised that the organic fraction of SSA may increase with decreasing particle size (Barker and Zeitlin, 1972; Hoffman and Duce, 1974). Three recent studies have examined this hypothesis. Oppo et al. (1999) constructed a simple model that predicted the surfactant organic fraction of SSA droplets will increase hyperbolic-like with decreasing droplet size. The model rests on the assumption that SSA droplets produced from the rough sea surface contain condensed, saturated films of surfactant material of constant thickness (independent of droplet size).

Experimentally, detailed measurements of the size-resolved organic fraction of SSA produced by flowing natural seawaters through bubble generators were conducted by Facchini et al. (2008) and Keene et al. (2007). A bubble generator mimics the bubble bursting process on ocean surfaces to generate nascent SSA isolated from other aerosol types. Both of these studies employed size-resolved impactor sampling and subsequent chemical analysis to show that SSA organic fraction increased with decreasing particle size in their experiments. Both studies measured an organic mass fraction of ~80% for the lowest stages of their impactor samples corresponding to aerodynamic diameters of 130 nm (GMD, Keene et al., 2007) and 125-250 nm (Facchini et al., 2008). However Keene et al. only measured soluble organics, and Facchini et al. measured both soluble and insoluble organics and found insoluble components dominate (~94% of organics). While both studies had different operative definitions of solubility, this consideration still implies that the results of these separate experiments do not agree as well as they first appear to. Nevertheless, based on these studies it is currently expected that the accumulation mode of SSA produced from biologically active seawater consists of particles that are predominantly organic. Bigg and Leck (2008) go even further to suggest that the particles comprising the SSA accumulation mode (< 200 nm) are actually organic fragments with no inorganic component at all.

It is important to characterise the composition of particles in the SSA accumulation mode to correctly model their climatic influence. The organic fraction of SSA particles will affect their size as a function of RH (Ming and Russell, 2001) and therefore their scattering potential (Randles et al., 2004), their ability to act as CCN (Moore et al., 2008) and also their role in atmospheric chemistry (Zhou et al., 2008). The purpose of this study was to investigate and quantify the organic fraction of bubble-chamber-generated accumulation mode SSA using an original, independent and on-line method: the Volatility Hygroscopicity- Tandem Differential Mobility Analyser (VH-TDMA). In addition the VH-TDMA was also able to measure the hygroscopic growth factors of SSA accumulation mode particles.

Experimental Methods

Bubble generator

A bubble generator was constructed to mimic the production of SSA by bursting bubbles on seawater surfaces. The generator is depicted in Figure 6.1. It consisted of a 1 m long glass cylinder (id = 2.9 cm) with a fritted glass tip (SKC midget impinger; pore size 170-220 μm) inserted at the bottom. Sample water entered the bottom of the generator from a 20 L plastic drum. The 20 L drum was placed above the generator so that gravity was the driving force of water through

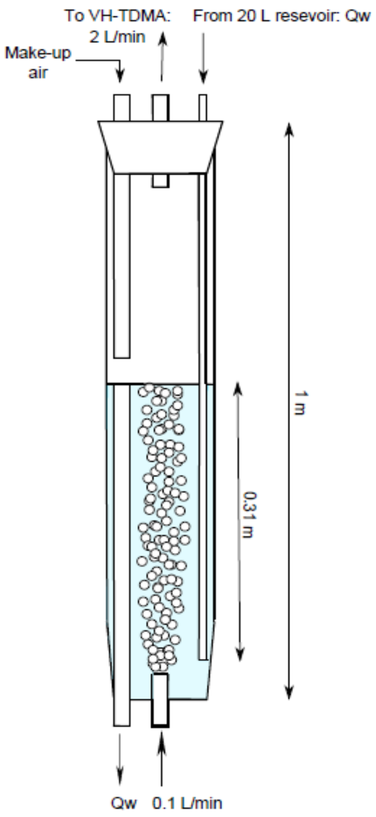


Figure 6.1: A schematic diagram of the bubble generator used to produce sea spray aerosol (SSA). Q_w is the water flow rate through the generator which was varied between experiments.

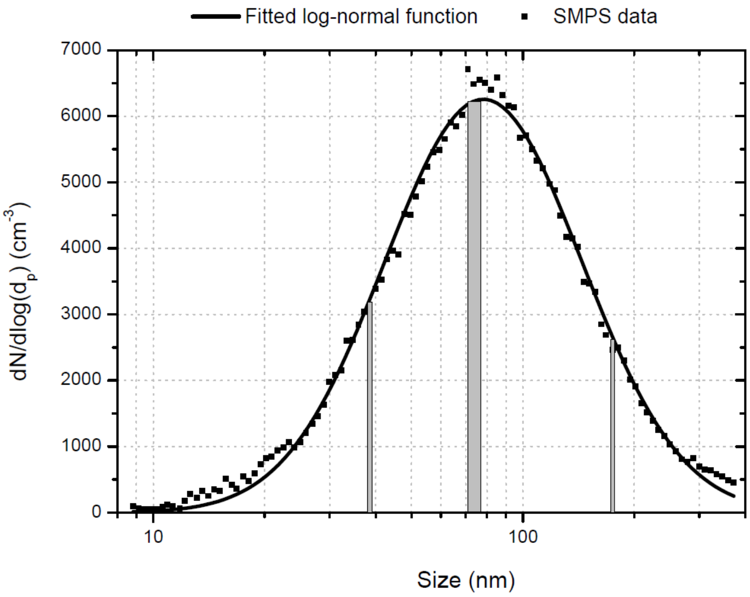


Figure 6.2: An SMPS size distribution (9–379 nm) of dry SSA produced from natural seawater in our bubble generator. Grey rectangles indicate particle sizes that were selected for VH-TDMA analysis.

the system. A tap was used to control the water flow rate. Water exited the generator through a 1/4 inch plastic tube fitted with a valve to prevent external air entering the generator. The vertical position of the exit tube was used to set the height of water in the generator. In these experiments the height was set for a bubble-rise distance of ~31 cm. This corresponded to a water volume of 200 mL. Particle-free air was bubbled through the fritted tip at a flow rate of 100 mL min^{-1} to produce a steady stream of bubbles. Bubble size distribution was not measured in these experiments. A sample outlet at the top of the generator was used to extract SSA produced by bursting bubbles at 2 L min^{-1} for VH-TDMA analysis. An inlet tube led from the top of the generator to just above the air-water interface to allow time for particle-free make-up air to mix with SSA before being sampled by the VH-TDMA. All experiments were conducted at room temperature (25°C) and SSA was dried (<10% RH) before it entered the VH-TDMA. The dry size distribution (9–379 nm) of SSA produced in our generator consisted of a dominant accumulation mode centred at ~80 nm (Figure 6.2), which compares well with other bubble-generated SSA size distributions (Martensson et al., 2003; Sellegri et al., 2006; Tyree et al., 2007).

Sample water

Experiments were conducted with two main types of water in the bubble generator: artificial sea salt solution (artificial SW) and natural seawater (natural SW). In addition the results were compared to VH-TDMA measurements of NaCl particles generated from an atomised solution of NaCl in ultra-pure deionised water. Artificial sea salt solution was generated by dissolving analytical grade sodium chloride (NaCl), magnesium chloride ($MgCl_2$), sodium sulphate (Na_2SO_4), calcium chloride ($CaCl_2$), potassium sulphate (K_2SO_4), sodium bromide (NaBr) and potassium nitrate (KNO_3) in ultra-pure deionised water. Two artificial salt solutions were prepared with varying ionic composition (Seinfeld and Pandis, 2006: pge. 444; Niedermeier et al., 2008).

Natural SW was collected at high tide on 28 January 2009 from Redcliffe Jetty, which extends 200 m into the north-western section of Moreton Bay on the east coast of Australia. Two minor river systems lie ~11 km to the north-west (Caboolture River) and ~8km to the south-west (Pine River) of the sampling site. As such the sampling site is subject to significant terrestrial run-off. The salinity of the collected samples was 31.8 g L^{-1}, measured via electrical conductivity (Eaton et al., 2005). The organic fraction or biological activity of our natural SW samples was not measured. However, monthly chlorophyll *a* (chl *a*) measurements (absorbance spectroscopy) at three sampling sites within a ~4 km radius of the sampling point were provided by the South East Queensland Healthy Waterways Partnership (www.healthywaterways.org). Chl *a* values at the three sites on 6-7 January 2009 varied between 1.47–3.14 mg m^{-3}. On 5 or 19 February 2009 chl *a* values at the three sites were in the range 1.29–3.21 mg m^{-3}. Therefore it is reasonable to assume that the biological activity of our natural SW samples was quite high. Dissolved organic carbon (DOC) content can vary widely in Moreton Bay depending, amongst other factors, on terrestrial run-off. Approximately 14 km north of Redcliffe Jetty in Moreton Bay, Albert et al. (2005) measured DOC concentrations of up to 50 mg L^{-1} during a wet period (large run-off) in 2003. In contrast DOC concentrations were only 10-20 mg L^{-1} during a dry period (small run-off) in 2002. Our sample collection was conducted in a relatively dry period (average monthly rainfall was low and similar to the average monthly rainfall during the Albert et al. measurements). Therefore we assume that the DOC content of our natural seawater was less than 20 mg L^{-1}. Natural SW samples were refrigerated in the dark and used within 2 weeks of the collection date. They were brought to room temperature and thoroughly stirred before bubbling experiments began.

Volatility Hygroscopicity-Tandem Differential Mobility Analyser (VH-TDMA)

The Volatility Hygroscopicity-Tandem Differential Mobility Analyser (VH-TDMA) has been described in detail elsewhere (Fletcher et al., 2007; Johnson et al., 2004; Modini et al., 2009) and will only be discussed very briefly here. The VH-TDMA was used to measure the average diameter of initially monodisperse SSA particles as they were heated in a thermodenuder (residence time = 0.3 secs) from ambient to 583°C in temperature increments of 15–60°C. Even after particle shrinkage occurred at higher temperatures the particles retained a monodisperse distribution. This means the average diameters before and after volatilisation could be used to calculate average volume fraction of SSA remaining (*V/Vo*). Volatility curves of different particle types were constructed by plotting *V/Vo* versus volatilisation temperature.

In addition, the VH-TDMA simultaneously measured the Hygroscopic Growth Factor at 90% RH ($HGF_{90\%}$) of the volatilised particles at each temperature. $HGF_{90\%}$ measurements of non-spherical particles taken with a (V)H-TDMA should be corrected for shape effects so they can be compared with independent measurements and theoretical predictions. The non-sphericity of dry NaCl particles is well described. For the range of NaCl particle sizes investigated in this study (65–98 nm) we applied a size-dependent shape correction factor that varied from 1.213–1.199 (Biskos et al., 2006). There is evidence to suggest that natural and artificial SSA particles are also non-spherical in shape and can be described with the same size-dependent shape correction factor as NaCl (Niedermeier et al., 2008; Wise et al., 2009). Therefore we also applied the NaCl shape correction factor to natural and artificial SSA particles in this study. To remove the influence of the Kelvin Effect on the $HGF_{90\%}$ measurements taken at different sizes they were converted to bulk $HGF_{90\%}$ values (i.e. where a_w=RH=0.9) using a constant single parameter representation of hygroscopic growth (Petters and Kreidenweis, 2007). The bulk $HGF_{90\%}$ values are reported here. All VH-TDMA data were inverted using the TDMAinv algorithm (Gysel et al., 2009). Assuming a DMA sizing accuracy of ±1% and RH uncertainty of ±0.6% the theoretical uncertainty (95% confidence level) is ±3% for *V/Vo* and ±3% for $HGF_{90\%}$.

Difference in the VH-TDMA volatility curves of natural and artificial SSA were used to investigate, and then quantify, the organic fraction of natural accumulation mode SSA. This approach is based on the assumptions that 1) natural SSA potentially contains a seawater-derived organic fraction that is not present in artificial SSA, 2) this organic fraction is more volatile than the inorganic fraction of SSA, 3) the inorganic composition of artificial and natural SWs used in these experiments is very similar, and 4) any organic impurities present in the artificial SSA were also present in the natural SSA. The third assumption was tested by using two types of artificial sea salt solution with varying inorganic composition so we could judge whether small differences in the inorganic composition of artificial SSA translated into measurable differences in the VH-TDMA volatility curves. The fourth assumption is considered a reasonable one because the pre-cleaning process of the bubble generator was constant for all experiments and artificial SW was prepared with ultra-pure deionised water.

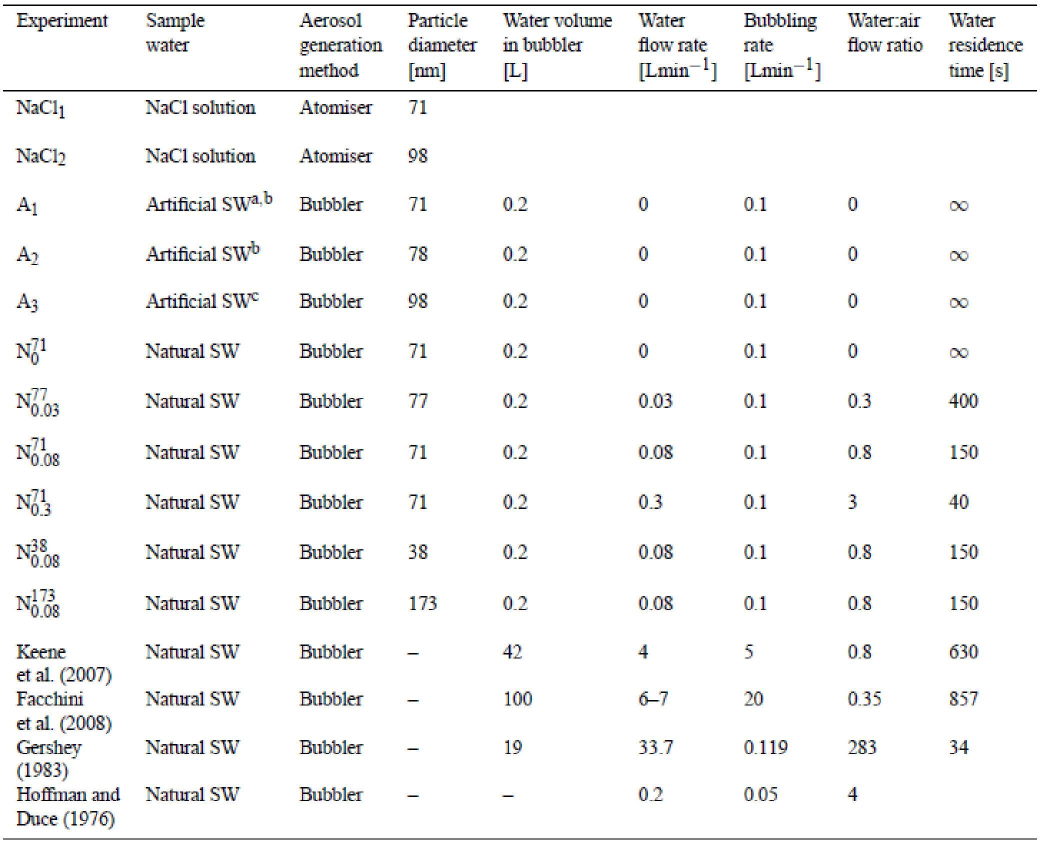
The advantages of using the VH-TDMA to measure the organic fraction of accumulation mode SSA are that only relatively small concentrations of particles (~100 cm^{-3}) are required for the analysis, total scan time is only 1-2 hrs and the lower size limit is ~10 nm. Therefore only a small bubble generator and sample of water are required (see Table 6.1), which reduces the chances of organic contamination. In addition, at RHs above the deliquescence point of SSA (~75%) organic components will decrease the hygroscopic growth factor of SSA (Ming and Russell, 2001). This means the $HGF_{90\%}$ measurements taken by the VH-TDMA can be used to confirm the conclusions drawn from the volatility measurements.

Experimental conditions

Table 6.1 lists the experiments we performed and values of important parameters compared to other studies that have utilised bubble generators. We chose to investigate whether the organic fraction of accumulation mode SSA particles depended on sample water flow rate through the bubble generator and SSA particle diameter. Water flow rate is important because if it is too low relative to the bubble flow rate (i.e. the organic source is less than the sink) then the organic content of sample water in the bubble generator could be depleted over time. The maximum water flow rate we used was 0.3 L min^{-1}. This value was large enough to ensure that the water:air flow ratio was higher and water residence time lower then studies where large concentrations of organics have been detected in the aerosol phase. At the other extreme we performed one experiment with static water in the bubble generator that was left to bubble for 24 hrs before a VH-TDMA scan was conducted.

The influence of particle size on organic fraction was investigated because, as stated above, previous studies have shown that the organic fraction of SSA increases with decreasing particle size (Facchini et al., 2008; Keene et al., 2007). Most VH-TDMA scans were performed on natural SSA particles 71–77 nm in mobility diameter because this was near the centre of the accumulation mode of SSA particles produced from our bubble generator, as measured by the VH-TDMA in scanning mobility particle sizer (SMPS) mode (Figure 6.2). In addition scans were also performed for particles towards the lower end (38 nm) and upper end (173 nm) of the SSA accumulation mode.

Table 6.1: Experimental parameters



Experiment	Sample water	Aerosol generation method	Particle diameter [nm]	Water volume in bubbler [L]	Water flow rate [$\mathrm{Lmin^{-1}}$]	Bubbling rate [$\mathrm{Lmin^{-1}}$]	Water:air flow ratio	Water residence time [s]
$\mathrm{NaCl_1}$	NaCl solution	Atomiser	71					
$\mathrm{NaCl_2}$	NaCl solution	Atomiser	98					
A_1	Artificial SW[a,b]	Bubbler	71	0.2	0	0.1	0	∞
A_2	Artificial SW[b]	Bubbler	78	0.2	0	0.1	0	∞
A_3	Artificial SW[c]	Bubbler	98	0.2	0	0.1	0	∞
N_0^{71}	Natural SW	Bubbler	71	0.2	0	0.1	0	∞
$N_{0.03}^{77}$	Natural SW	Bubbler	77	0.2	0.03	0.1	0.3	400
$N_{0.08}^{71}$	Natural SW	Bubbler	71	0.2	0.08	0.1	0.8	150
$N_{0.3}^{71}$	Natural SW	Bubbler	71	0.2	0.3	0.1	3	40
$N_{0.08}^{38}$	Natural SW	Bubbler	38	0.2	0.08	0.1	0.8	150
$N_{0.08}^{173}$	Natural SW	Bubbler	173	0.2	0.08	0.1	0.8	150
Keene et al. (2007)	Natural SW	Bubbler	–	42	4	5	0.8	630
Facchini et al. (2008)	Natural SW	Bubbler	–	100	6–7	20	0.35	857
Gershey (1983)	Natural SW	Bubbler	–	19	33.7	0.119	283	34
Hoffman and Duce (1976)	Natural SW	Bubbler	–	–	0.2	0.05	4	

[a] This experiment is the average of 3 almost indistinguishable repeated scans
[b] Ionic mass fractions according to Seinfeld and Pandis (1998), page 444
[c] Ionic mass fractions according to Niedermeier et al. (2008), Atlantic Ocean sample

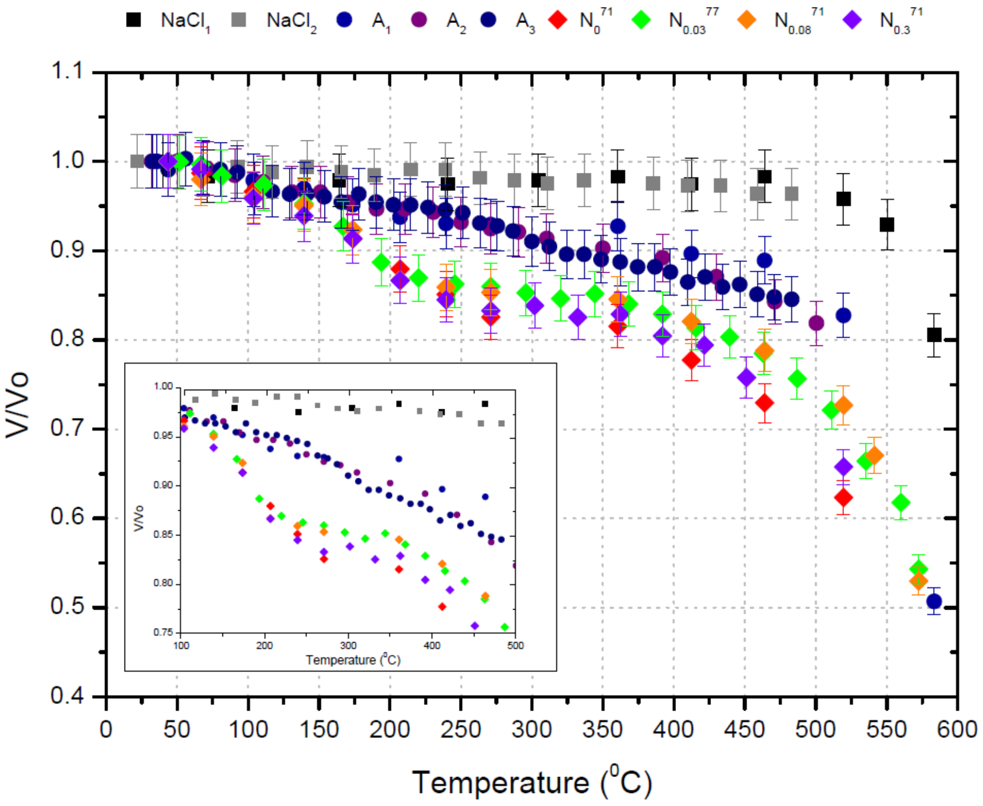


Figure 6.3: Volatility curves of NaCl (squares), artificial SSA particles (circles) and 71–77 nm natural SSA particles (diamonds) generated using different water flow rates. Legend notation is described in text and Table 1. Error bars represent ±3% measurement uncertainty in *V/Vo*. Inset graph is magnified version of main graph with error bars removed.

Results and Discussion

VH-TDMA volatility curves

The organic fraction of 71–77 nm natural SSA particles

Figure 6.3 displays the N_0^{71}, $N_{0.03}^{77}$, $N_{0.08}^{71}$ and $N_{0.3}^{71}$ volatility curves as measured by the VH-TDMA. In this notation N refers to natural SSA particles, the subscript number refers to the sample water flow rate through the bubble generator in L min^{-1} and the superscript number refers to the particle mobility diameter in nm (see Table 6.1). In addition the A_1, A_2, A_3, $NaCl_1$ and $NaCl_2$ volatility curves are included for comparison (the subscript number here is simply an index). The NaCl particles (square markers) were very stable as volatilisation temperature was increased. A significant decrease in *V/Vo* was only observed at the highest temperature obtained in these experiments, 583°C. This sudden decrease indicated evaporation of NaCl had begun, which is consistent with the onset temperature for particle formation in evaporation/condensation NaCl aerosol generation experiments (Scheibel and Porstendo¨rfer, 1983). The artificial SSA particles (circle markers) were more volatile than the pure NaCl particles. Artificial SSA *V/Vo* decreased fairly steadily as temperature increased so that only 82-83% of particle volume remained at 520°C. In contrast 96% of NaCl particle volume remained at this temperature. The increased volatility of artificial SSA compared to NaCl particles could be because the evaporation or melting point of the mixture of inorganic salts was lower than the equivalent point for any pure salt in that mixture. The volatility curves of all three artificial SSA experiments agreed within the *V/Vo* measurement uncertainty. This indicates that small differences in the size and inorganic composition of artificial SSA does not translate into significant changes in the volatility curves, which confirms assumption number 3 of our VH-TDMA measurement approach.

The 71–77 nm natural SSA particles (diamond markers) were even more volatile than the artificial SSA particles. The natural SSA volatility curves began to diverge from the artificial SSA curves at 170°C (see inset, Fig. 6.3). A small step in the volatilisation curves was observed before they began to level out at 200°C. Beyond this temperature the volatility curves of natural and artificial SSA became very similar in shape and appear almost parallel. The natural SSA particles were expected to contain a seawater-derived organic component not present in artificial SSA. We contend that in the temperature range 170–200°C the organic component of natural SSA evaporated in the VH-TDMA. Beyond this temperature the similarity of the volatility curves and point where complete evaporation begins (~575°C) for natural and artificial SSA is consistent with the explanation that they now have similar, predominantly inorganic composition. The average difference between the artificial and natural SSA volatility curves in the temperature range 200–500°C can then be taken as a measure of the average organic volume fraction of the 71–77 nm natural SSA particles. This average difference was 8%. The standard deviation of the difference was 2% and the theoretical uncertainty was 6% (twice the *V/Vo* measurement error). We take the larger value of ±6% as the absolute error in the measured organic volume fraction of 8%.

Dependence of organic fraction on water flow rate through the bubble generator

The volatility curves of 71–77 nm natural SSA particles generated under varying water flow rates agreed almost completely within measurement uncertainty. That is, the organic fraction of 71–77 nm natural SSA particles produced in our generator did not depend on water flow rate. If anything, the N_0^{71} curve lies slightly below all others. This indicates that the rate of transfer of organic material out of our bubble generator by SSA is not sufficient to deplete the organic content of a 200 mL sample of natural SW, even after it has been bubbling at 100 mL min^{-1} for 24 hrs. This is consistent with calculations of the amount of organic material exported by SSA from seawater in the bubble generator. As well as the measured accumulation mode (see Fig. 6.2) there should have been a second super-micrometer mode in our SSA size distribution (e.g. Keene et al., 2007; Martensson et al., 2003). Therefore, we assumed a bi-modal distribution with certain properties (accumulation mode: median diameter = 0.08 μm, concentration = 10 000 cm^{-3}, organic mass fraction = 80%; super-micrometer mode: median diameter = 4 μm, concentration = 200 cm^{-3}, organic mass fraction = 10%) and an organic density of 1.1 g cm^{-3} (Keene et al., 2007). Although we didn’t measure such large organic fractions in this study we purposely overestimated them for this calculation. Under these assumptions and the conditions of our bubbling experiments only 2 x 10^{-4} g day^{-1} of organic material would be exported by SSA from our sample water. If we assume the organic content of our 200 mL sample of seawater was only 1 mg L^{-1}, it would take 23 hours of SSA generation to deplete all the organics in the water. If we assume the seawater organic concentration was 10 mg L^{-1}, full depletion would take 234 hours. The fact that organics were not depleted in our generator after bubbling for 24 hrs suggests that the organic content of our sample water was greater than 1 mg L^{-1}, or that we have overestimated the number and organic fraction of super-micrometer SSA particles in this calculation.

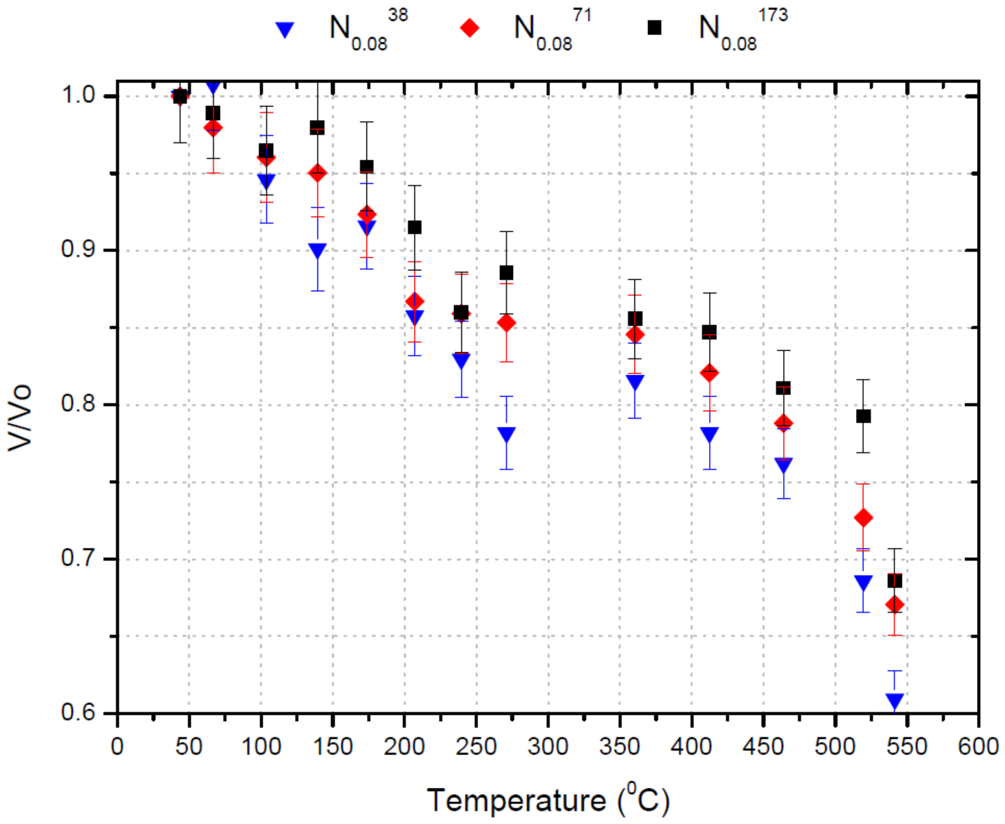


Figure 6.4: Volatility curves of 38 nm (upside down triangles), 71 nm (diamonds) and 173 nm (squares) natural SSA particles. Legend notation is described in text and Table 1. Error bars represent ±3% measurement uncertainty in *V/Vo*.

Dependence of organic fraction on particle size in the range 38–173 nm

Figure 6.4 displays the 38 nm ($N_{0.08}{}^{38}$), 71 nm ($N_{0.08}{}^{71}$) and 173 nm ($N_{0.08}{}^{173}$) volatility curves. It appears that volatility increased slightly with decreasing particle size. In the temperature range 200–500°C where it is expected that the organic fraction of the particles has evaporated the average difference (±1 standard deviation) between the 173 nm and 38 nm curves is 6±3%. The average difference between the 173 nm and 71 nm curves and the 71 nm and 38 nm curves in the same range is 2±2% and 3±2%, respectively. However, these volatility differences could be due to differences in particle size as well as composition (organic fraction). Therefore these values do not represent the difference in organic volume fraction for the different particles sizes. Rather they overestimate these fractions by an unknown amount equal to the percentage change in *V/Vo* due to the change in initial particle size. Taking this into account and the fact that the theoretical uncertainty in the calculation of organic volume fraction is 6%, we conclude that the organic fraction of natural SSA particles did not vary significantly with particle mobility diameter in the range 38–173 nm.

Hygroscopic growth factor measurements

To improve the representation of the shape- and Kelvin-corrected bulk $HGF_{90\%}$ data all of the measurements were first categorised as NaCl, artificial SSA or natural SSA (71–77 nm) particles. Then a number of measurements were averaged at specific temperature values to obtain average $HGF_{90\%}$ for each particle type as a function of temperature. These averages are plotted in Figure 6.5. At ambient temperature NaCl $HGF_{90\%}$ was 2.46±0.02. Artificial SSA $HGF_{90\%}$ was 4.4% lower at 2.35±0.02. These values both agree well with theoretical predictions of NaCl and artificial SSA $HGF_{90\%}$ (e.g. Ming and Russell, 2001). Natural SSA $HGF_{90\%}$ was 3.9% lower than artificial SSA (8.1% lower than NaCl) at 2.26±0.02.

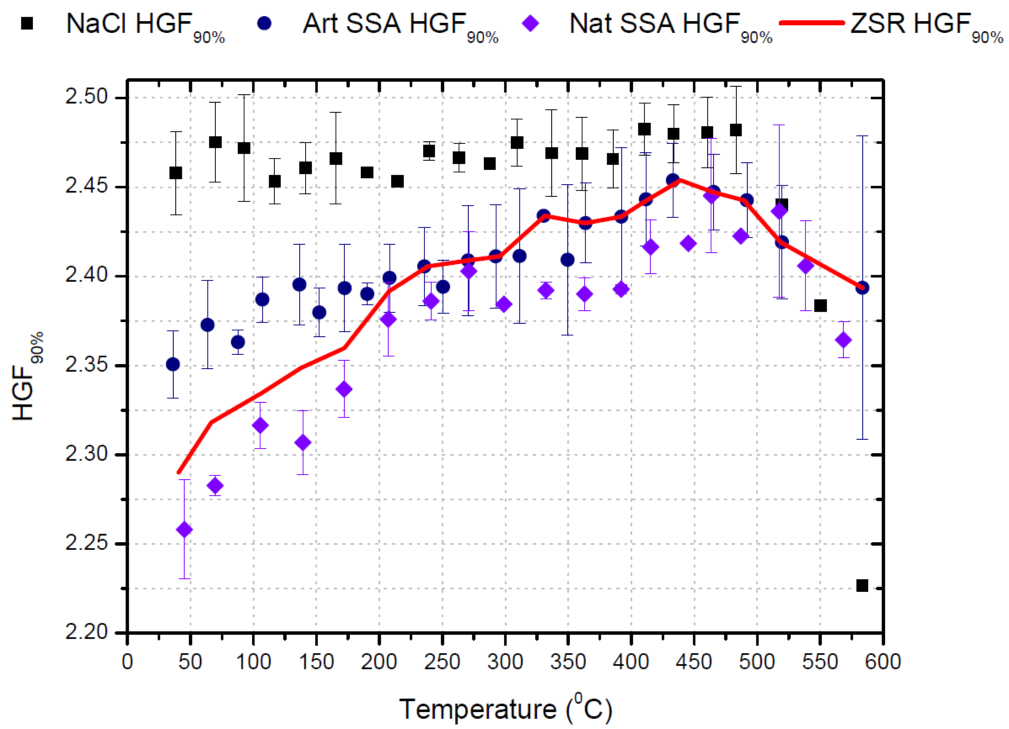


Figure 6.5: Shape- and Kelvin-corrected bulk $HGF_{90\%}$ values for NaCl (squares), artificial SSA (circles) and natural SSA (diamonds) particles as a function of volatilisation temperature. Each data point represents an average of a number of measurements and error bars represent ±1 standard deviation. Measurement uncertainty in $HGF_{90\%}$ was ±3%. Also included is the ZSR predicted $HGF_{90\%}$ curve (solid red line). See text for details on the calculation of this curve.

It is instructive to observe how $HGF_{90\%}$ for each particle type varied as a function of temperature. NaCl $HGF_{90\%}$ was fairly constant until particle evaporation began at the highest temperatures. At this point NaCl $HGF_{90\%}$ decreased. Artificial SSA $HGF_{90\%}$ continually increased with increasing volatilisation temperature. Natural SSA $HGF_{90\%}$ was below artificial SSA $HGF_{90\%}$ up to a volatilisation temperature of 170°C. At this temperature the organic component of the natural SSA particles began evaporating (see Figure 6.3). Coinciding with this the $HGF_{90\%}$ curve started approaching the artificial SSA $HGF_{90\%}$ curve. At temperatures above 206°C the artificial and natural $HGF_{90\%}$ curves agreed almost completely within experimental variation. The shapes of the two curves were even very similar.

Under the ZSR approximation (Chen et al., 1973; Stokes and Robinson, 1966) it is possible to investigate whether the difference in the natural and artificial SSA

$HGF_{90\%}$ curves at lower temperatures is consistent with the volume fraction of organics in the natural SSA particles as calculated from the volatility data (see section 3.1.1). When making the ZSR approximation it is assumed that the individual components of an internally mixed particle do not interact with each other and therefore they uptake water independently. In practice this means that the *HGF* of a mixed particle can be calculated by the volume-fraction-weighted sum of the *HGF's* of individual components in that particle. We can use this assumption to predict $HGF_{90\%}$ for our natural SSA particles assuming they are a binary mixture of an organic and inorganic (sea salt) component. For input into the ZSR approximation we use our measured organic volume fraction as a function of temperature, our measured bulk $HGF_{90\%}$ of artificial SSA as a function of temperature and assume a bulk $HGF_{90\%}$ for the organic component of 1. This leads to a ZSR predicted $HGF_{90\%}$ curve which is plotted in Figure 6.5. There is generally good agreement between the ZSR predicted and measured natural SSA $HGF_{90\%}$ curves. At temperatures less than 200°C the ZSR predicted curve only slightly overestimates the measurements. At temperatures greater than 200°C the ZSR predicted $HGF_{90\%}$ curve equals the artificial $HGF_{90\%}$ curve because it is assumed that all organics have evaporated from the natural SSA particles and organic volume fraction is set to 0 (Fig. 6.3).

In summary, the $HGF_{90\%}$ data are consistent with the conclusions drawn from the volatility data. Namely, that our natural SSA particles had a minor organic component that evaporated over the temperature range 170–200°C. After evaporation the natural and artificial SSA particles had similar, predominantly inorganic composition.

Implications

We have measured an organic volume fraction of 8±6% for 71–77 nm natural SSA particles that were generated from samples of coastal seawater that most likely had high organic content. Note that this means aerosol-phase organics were still enriched by tens or hundreds of times relative to the sample water, depending on the exact concentration of organics in the sample water. Assuming an organic density of 1.1 g cm^{-3} (Keene et al., 2007) our measurement corresponds to an organic mass fraction of only 4%. We also investigated the organic fractions of 38 and 173 nm natural SSA particles and found these did not differ significantly from the organic fraction of 71–77 nm particles. In comparison, Keene et al. (2007) measured an organic mass fraction of ~80% for 130 nm (GMD) natural SSA particles in similar bubbling experiments. Facchini et al. (2008) measured an organic fraction of 77±5% for 125–250 nm natural SSA particles. These findings have led to the expectation that accumulation mode SSA particles generated from biologically active or organic-rich seawaters are predominantly organic. Our results suggest that this is not always the case.

Hygroscopicity measurements in the literature also provide indirect evidence that accumulation mode SSA particles often contain only a minor organic fraction. Sea salt aerosol (i.e. purely inorganic) is very hygroscopic. If a major, non-hygroscopic organic fraction is present in SSA it will significantly decrease the hygroscopicity of that aerosol. For example an SSA particle consisting of 20% sea salt ($HGF_{90\%}$ = 2.35) and 80% organics ($HGF_{90\%}$ = 1) will have $HGF_{90\%}$ = 1.5 according to the ZSR approximation. A few studies have reported *HGF's* above deliquescence RH for accumulation mode natural SSA particles that are only slightly below (< 10%) corresponding NaCl or sea salt *HGF's* (Niedermeier et al., 2008; Sellegri et al., 2008; Swietlicki et al., 2008). This suggests the natural SSA particles investigated in these studies did not contain large organic fractions. In a very recent study Herich et al. (2009) detected an organic component in both fresh and aged 260 nm SSA particles at a remote continental site in the arctic circle in northern Sweden. The authors found that SSA organic content did not correlate with SSA hygroscopicity. This implies that the organic component only formed a very minor fraction of total SSA mass, because changes in the amount of organics present had no effect on particle hygroscopicity. Although these studies do not report measurements (e.g. organic content, biological activity) of the source water from which aerosols were generated, they nevertheless suggest that accumulation mode SSA frequently contains only a minor organic fraction.

Discrepancies between the different studies could be related to not only the amount of organics present in the source waters used in each experiment, but also the composition and surface-active nature of those organics. For example Facchini et al. (2008) conducted their measurements with organic-rich Atlantic Ocean water collected during a plankton bloom. The Keene et al. (2007) results were obtained using seawater collected from a Bermuda passage (Ferry Reach). Measurements indicated the water was representative of the surrounding oligotrophic open ocean surface water. Our measurements were conducted with organic-rich seawater, but this time collected at a coastal site significantly affected by terrestrial run-off. The difference in the composition of organics (anthropogenic or biogenic, coastal or open ocean) may affect how enriched they become in the aerosol phase. We are not aware of any studies that have examined the relationship between seawater type and SSA organic fraction. Therefore it is not clear what effect, if any, the use of coastal as opposed to ocean seawater had on the SSA organic fraction measured in this study.

In addition to seawater type, methodological differences could have potentially contributed to some of the difference between the results of this study and the results of the Keene and Facchini studies. The two previous studies were conducted with freshly-collected seawater while in this study seawater was stored in a dark refrigerator for up to 2 weeks. The properties of seawater organics may have changed during this storage time which could have affected their transfer to the aerosol phase. However, we note that no significant differences were observed between scans completed at different times during the 2 week measurement period. Therefore any artefacts due to storage are likely to be minimal. The bubble generator employed in this study was also far smaller than those used in previous studies (see water volumes in Table 6.1). While this reduced the risk of external organic contamination, it also meant our generator had a high surface to volume ratio. As seawater flowed bottom-to-top in the generator organics potentially adsorbed to the walls thereby reducing the amount of organics eventually transferred to the aerosol. This potential loss mechanism was not quantified or estimated. We do not believe that these methodological differences can account for the order of magnitude difference between our measured accumulation mode SSA organic fraction and the fractions measured in the Keene and Facchini studies.

O'Dowd et al. (2008) have developed a combined organic-inorganic sub-micron sea spray source function for modelling purposes. One input into this source function is the organic mass fraction of sub-micron SSA as a function of chl *a* concentration, which was derived from ambient measurements conducted at Mace Head, Ireland. This function saturates at 90% organic mass fraction for chl *a* concentrations above 1.27 mg m^{-3}. Chl *a* concentration was at least this high, and probably higher, in the seawater used in this study. However, the organic mass fraction of accumulation mode SSA was only 4%. This suggests that the sub-micron SSA organic fractions predicted by the O’Dowd et al. source function may be significant overestimates of the true values in regions other than off the coast of Mace Head.

These considerations point to the need for further independent, size-resolved measurements of the organic fraction of SSA produced from a variety of different seawaters. Based on the conflicting studies, it seems that there may be some additional properties of seawater (e.g. organic composition, surface-active nature of organics) that control how much organic material is transported from water to the aerosol phase during the bubble bursting process. In addition, our results suggest that if these experiments are conducted with bubble generators, it may not be necessary to cycle water through the generator to maintain a fresh supply of seawater-organics. Bubble-generated SSA did not deplete the organic content of static seawater in our bubble generator over a 24 hr period.

Conclusion

A bubble generator was constructed and used to produce SSA particles from samples of coastal seawater collected from Moreton Bay on the east coast of Australia. Chlorophyll *a* measurements conducted close to the sampling point on either side of the collection date indicated that the samples were biologically active and had high organic content. A VH-TDMA was used to investigate the organic fraction of accumulation mode SSA particles produced from bubbling the seawater in the generator. The volatility and hygroscopic data collected by the VH-TDMA were in good agreement with each other, and suggested that the natural SSA particles contained an organic component that evaporated in the range 170–200°C. A comparison between the volatility curves of artificial and natural SSA particles was used to quantify the organic fraction of 71–77 nm natural SSA particles at 8±6%. This measurement is an order of magnitude below comparable previous measurements of the organic fraction of accumulation mode SSA. At room temperature we measured shape- and Kelvin-corrected growth factors at 90% RH of 2.46±0.02 for NaCl, 2.35±0.02 for artifical SSA and 2.26±0.02 for natural SSA particles. We reiterate that our results apply to accumulation mode SSA generated from coastal as opposed to open ocean seawater.

Acknowledgements

This work was funded by the International Laboratory for Air Quality and Health. The authors gratefully acknowledge the South East Queensland Healthy Waterways Partnership (www.healthywaterways.org) for provision of the chlorophyll *a* data for Moreton Bay.

References

Albert, S., O'Neil, J. M., Udy, J. W., Ahern, K. S., O'Sullivan, C. M., and Dennison, W. C.: Blooms of the cyanobacterium Lyngbya majuscula in coastal Queensland, Australia: disparate sites, common factors, Mar. Pollut. Bull., 51, 428-437, 2005.

Andreae, M. O., and Rosenfeld, D.: Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, Earth-Science Reviews, 89, 13-41, 2008.

Barker, D. R., and Zeitlin, H.: Metal-Ion Concentrations in Sea-Surface Microlayer and Size-Separated Atmospheric Aerosol Samples in Hawaii, J. Geophys. Res., 77(27), 5076-5086, 1972.

Bigg, E. K., and Leck, C.: The composition of fragments of bubbles bursting at the ocean surface, J. Geophys. Res., 113, D11209, doi:10.1029/2007JD009078, 2008.

Biskos, G., Russell, L. M., Buseck, P. R., and Martin, S. T.: Nanosize effect on the hygroscopic growth factor of aerosol particles, Geophys. Res. Lett., 33, L07801, doi:10.1029/2005GL025199, 2006.

Blanchard, D. C.: Sea-to-Air Transport of Surface Active Material, Science, 146, 396-397, 10.1126/science.146.3642.396, 1964.

Blanchard, D. C.: The ejection of drops from the sea their enrichment with bacteria and other materials: A review, Estuaries, 12, 127-137, 1989.

Chen, H., Sangster, J., Teng, T. T., and Lenzi, F.: A general method of predicting the water activity of ternary aqueous solutions from binary data, Can. J. Chem. Eng., 51, 234-241, 1973.

Clarke, A. D., Owens, S. R., and Zhou, J.: An ultrafine sea-salt flux from breaking waves: Implications for cloud condensation nuclei in the remote marine atmosphere, J. Geophys. Res., 111, D06202, doi:10.1029/2005JD006565, 2006.

Eaton, A. D., Clesceri, L. S., Rice, E. W., and Greenberg, A. E.: Standard methods for the examination of water and wastewater, American Public Health Association, American Water Works Association, Water Environment Federation, Section 2520B, 2005.

Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, L17814, doi:10.1029/2008GL034210, 2008.

Fletcher, C. A., Johnson, G. R., Ristovski, Z. D., and Harvey, M.: Hygroscopic and volatile properties of marine aerosol observed at Cape Grim during the P2P campaign, Environ. Chem., 4, 162-171, 2007.

Gershey, R. M.: Characterization of seawater organic matter carried by bubble-generated aerosols, Limnol. Oceanogr., 28, 309-319, 1983.

Gysel, M., McFiggans, G. B., and Coe, H.: Inversion of tandem differential mobility analyser (TDMA) measurements, J. Aerosol Sci., 40, 134-151, 2009.

Herich, H., Kammermann, L., Friedman, B., Gross, D. S., Weingartner, E., Lohmann, U., Spichtinger, P., Gysel, M., Baltensperger, U., and Cziczo, D. J.: Subarctic atmospheric aerosol composition: 2. Hygroscopic growth properties, J. Geophys. Res., 114, D13204, doi:10.1029/2008JD011574, 2009.

Hoffman, E. J., and Duce, R. A.: The Organic Carbon Content of Marine Aerosols Collected on Bermuda, J. Geophys. Res., 79(30), 4474-4477, 1974.

Hoffman, E. J., and Duce, R. A.: Factors Influencing the Organic Carbon Content of Marine Aerosols: A Laboratory Study, J. Geophys. Res., 81(21), 3667-3670, 1976.

Hunter, K. A.: Chemistry of the sea-surface microlayer, in: The sea surface and global change, edited by: Liss, P. S., and Duce, R. D., Cambridge University Press, Cambridge, UK, 287-321, 1997.

Johnson, G. R., Ristovski, Z., and Morawska, L.: Method for measuring the hygroscopic behaviour of lower volatiliy fractions in an internally mixed aerosol, J. Aerosol Sci., 35, 443-455, 2004.

Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl, E. E., Izaguirre, M. A., Davis, A. J., Long, M. S., Zhou, X., Smoydzin, L., and Sander, R.: Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface, J. Geophys. Res., 112, D21202, doi:10.1029/2007JD008464, 2007.

Liss, P. S., and Duce, R. D.: The sea surface and global change, Cambridge University Press, Cambridge, UK, 1997.

Martensson, E. M., Nilsson, E. D., de Leeuw, G., Cohen, L. H., and Hansson, H. C.: Laboratory simulations and parameterization of the primary marine aerosol production, J. Geophys. Res., 108 (D9), 4297, doi:10.1029/2002JD002263, 2003.

Ming, Y., and Russell, L. M.: Predicted hygroscopic growth of sea salt aerosol, J. Geophys. Res., 106(D22), 28259-28274, 2001.

Modini, R. L., Ristovski, Z. D., Johnson, G. R., He, C., Surawski, N., Morawska, L., Suni, T., and Kulmala, M.: New particle formation and growth at a remote, sub-tropical coastal location, Atmos. Chem. Phys., 9, 7607-7621, 2009.

Moore, R. H., Ingall, E. D., Sorooshian, A., and Nenes, A.: Molar mass, surface tension, and droplet growth kinetics of marine organics from measurements of CCN activity, Geophys. Res. Lett., 35, L07801, 10.1029/2008gl033350, 2008.

Niedermeier, D., Wex, H., Voigtländer, J., Stratmann, F., Brüggemann, E., Kiselev, A., Henk, H., and Heintzenberg, J.: LACIS-measurements and parameterization of sea-salt particle hygroscopic growth and activation, Atmos. Chem. Phys., 8, 579-590, 2008.

O'Dowd, C. D., and Smith, M. H.: Physicochemical Properties of Aerosols Over the Northeast Atlantic: Evidence for Wind-Speed-Related Submicron Sea-Salt Aerosol Production, J. Geophys. Res., 98(D1), 1137-1149, 1993.

O'Dowd, C. D., Smith, M. H., Consterdine, I. E., and Lowe, J. A.: Marine aerosol, sea-salt, and the marine sulphur cycle: a short review, Atmos. Env., 31, 73-80, 1997.

O'Dowd, C. D., Langmann, B., Varghese, S., Scannell, C., Ceburnis, D., and Facchini, M. C.: A combined organic-inorganic sea-spray source function, Geophys. Res. Lett., 35, L01801, doi:10.1029/2007GL030331, 2008.

Oppo, C., Bellandi, S., Degli Innocenti, N., Stortini, A. M., Loglio, G., Schiavuta, E., and Cini, R.: Surfactant components of marine organic matter as agents for biogeochemical fractionation and pollutant transport via marine aerosols, Mar. Chem., 63, 235-253, 1999.

Petters, M. D., and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, 2007.

Pierce, J. R., and Adams, P. J.: Global evaluation of CCN formation by direct emission of sea salt and growth of ultrafine sea salt, J. Geophys. Res., 111, D06203, doi:10.1029/2005JD006186, 2006.

Randles, C. A., Russell, L. M., and Ramaswamy, V.: Hygroscopic and optical properties of organic sea salt aerosol and consequences for climate forcing, Geophys. Res. Lett., 31, L16108, doi:10.1029/2004GL020628, 2004.

Scheibel, H. G., and Porstendo¨rfer, J.: Generation of monodisperse Ag- and NaCl-aerosols with particle diameters between 2 and 300 nm, Journal of Aerosol Science, 14, 113-126, 1983.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics : from air pollution to climate change, 2nd ed., Wiley, Hoboken, N.J., p. 444, 2006.

Sellegri, K., O'Dowd, C. D., Yoon, Y. J., Jennings, S. G., and de Leeuw, G.: Surfactants and submicron sea spray generation, J. Geophys. Res., 111, D22215, doi:10.1029/2005JD006658, 2006.

Sellegri, K., Villani, P., Picard, D., Dupuy, R., O'Dowd, C., and Laj, P.: Role of the volatile fraction of submicron marine aerosol on its hygroscopic properties, Atmospheric Research, 90, 272-277, 2008.

Spiel, D. E.: On the births of jet drops from bubbles bursting on water surfaces, J. Geophys. Res., 100(C3), 4995-5006, 1995.

Spiel, D. E.: On the births of film drops from bubbles bursting on seawater surfaces, J. Geophys. Res., 103(C11), 24907-24918, 1998.

Stokes, R. H., and Robinson, R. A.: Interactions in Aqueous Nonelectrolyte Solutions. I. Solute-Solvent Equilibria, The Journal of Physical Chemistry, 70, 2126-2131, 1966.

Swietlicki, E., Hansson, H.-C., HÄMeri, K., Svenningsson, B., Massling, A., McFiggans, G. B., Mcmurry, P. H., PetÄJÄ, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., and Kulmala, M.: Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments: a review, Tellus B, 60, 432-469, 2008.

Tyree, C. A., Hellion, V. M., Alexandrova, O. A., and Allen, J. O.: Foam droplets generated from natural and artificial seawaters, J. Geophys. Res., 112, D12204, doi:10.1029/2006JD007729, 2007.

Wise, M. E., Freney, E. J., Tyree, C. A., Allen, J. O., Martin, S. T., Russell, L. M., and Buseck, P. R.: Hygroscopic behavior and liquid-layer composition of aerosol particles generated from natural and artificial seawater, J. Geophys. Res., 114, D03201, doi:10.1029/2008JD010449, 2009.

Zhou, X., Davis, A. J., Kieber, D. J., Keene, W. C., Maben, J. R., Maring, H., Dahl, E. E., Izaguirre, M. A., Sander, R., and Smoydzyn, L.: Photochemical production of hydroxyl radical and hydroperoxides in water extracts of nascent marine aerosols produced by bursting bubbles from Sargasso seawater, Geophys. Res. Lett., 35, L20803, doi:10.1029/2008GL035418, 2008.

Chapter 7: Closing discussion

7.1 General comments

This research program has contributed significantly to the scientific knowledge of marine aerosols and the way they interact with water vapour. Marine aerosols are loosely defined as particles suspended over the oceans. Oceans cover more than 70% of the Earth's surface so this provides an enormous area over which particles scatter and absorb radiation and act as the seeds upon which cloud droplets form. Thus, marine aerosols are major players in the changing global climate system and this warrants our investigation of them.

The primary aim of this research was to investigate how organic components can influence the water uptake properties of marine aerosols. To this end investigations were made on the formation, composition and hygroscopic properties of both primary and secondary marine aerosols. In particular, field campaigns were conducted at 2 coastal locations and laboratory bubble-chamber measurements were performed with natural seawater samples. The main instrument employed throughout the program was the Volatility-Hygroscopicity-TDMA (VH-TDMA). This was used to investigate the effect that volatile organic components had on the hygroscopic growth of multi-component marine aerosol particles. It was also used to make inferences regarding the chemical composition of these particles. A number of interesting and original insights were obtained during the program relating to coastal nucleation events, water uptake suppression by organics, additional VH-TDMA developments and accumulation mode sea spray particles. These findings and their significance are explained in more detail below.

7.2 Specific findings of significance

7.2.1 Coastal nucleation events: Chapter 3

- New particle formation and growth events were observed for the first time at Agnes Water. They occurred on 65% of the days during a month-long measurement campaign. Although it is possible that the precursor vapours responsible for particle formation and growth came from the continent, it was judged much more likely that they were of marine/coastal origin. In particular, the biologically rich waters of Hervey Bay and the coastal area of Fraser Island were identified as likely source regions for the particle precursors.

- Similarly to other coastal nucleation studies, the Agnes Water events occurred when solar intensity was high and relative humidity was low. This indicated that photo-chemical oxidation processes were an important stage in the new particle formation process. However, unlike most other studies the events had no relation to tide height either at the measurement site or at an upwind coastal location (Fraser Island). Natural coastal particle production that is not related to tide height has only been observed at 2 other locations; Lizard Island, Australia (Leck and Bigg, 2008) and Bodega Bay, California (Wen et al., 2006). Therefore, this is an important observation because it adds to the scarce evidence that coastal particle production can result from processes other than the emission of precursor vapours from marine biota exposed at low tide.

- The growth rates of particles and ions during the Agnes Water nucleation events were calculated and published. This is useful data for comparison with nucleation studies at other sites around the world.

- A unique component of the Agnes Water study was the investigation of the chemical composition of freshly nucleated particles (d_p 17-22.5 nm) with a VH-TDMA. The majority of the volume of these particles was confidently attributed to sulphate and organic components. This was a significant result because very few studies have been able to probe the composition of atmospheric nucleation mode particles. The lower size limit of the VH-TDMA in the Agnes Water study was ~10 nm. Therefore, based on this compositional data we were unable to determine whether iodine- or sulphate-mediated particle formation occurred, even though we obtained no evidence for the existence of iodine-containing compounds in 17-22.5 nm particles. However, we were able to conclude that nucleation mode particles grew by the condensation of sulphate and/or organic vapours. It is important to understand this growth process because it determines whether freshly formed particles are able to grow into the Aitken mode and beyond where they can participate in the direct and indirect effects of aerosols on climate.

- In addition, the first direct evidence of secondary particle production from the Great Barrier Reef (GBR) was obtained during the Agnes Water study. This came in the form of a particularly strong and long-lasting nucleation event that occurred on the one day throughout the entire campaign that air masses passed over the southernmost reefs of the GBR before arriving at the sampling point. Particles grew quickly to ~80 nm in diameter during the day-long event. If it is assumed that similarly intense particle production occurs regularly along the whole 2600 km length of the GBR then it would constitute a major, natural source of ultrafine particles and CCN. This would make the GBR a significant regulator of the regional climate, which is particularly interesting considering it is expected to undergo serious change as temperatures increase due to global warming.

7.2.2 Water uptake suppression: Chapter 4

- Internally mixed multi-component particles were detected in 9 out of 18 VH-TDMA scans conducted on nucleation and Aitken mode particles sampled in clean marine air at the Agnes Water site. A variable labelled water uptake ratio (WUR) was (re)introduced and calculated for each VH-TDMA scan to explicitly examine the effect that volatile organic components had on the hygroscopic growth of the multi-component particles.

- Organic components that significantly suppressed the hygroscopic growth of Aitken mode particles were detected in 3 scans conducted on 2 separate days. Two possible mechanisms were suggested to explain the water uptake suppression; a kinetic mechanism involving the existence of organic films that inhibited the rate of water uptake and a thermodynamic mechanism involving interactions between organic and inorganic components in solution that had a negative effect on hygroscopicity. Both mechanisms are worthy of further investigation. If the kinetic mechanism is most relevant than it will affect the ability of particles to activate as CCN in the finite time supersaturation is maintained in a rising air mass. If the thermodynamic mechanism is most relevant than this has implications for our ability to predict the water uptake of atmospheric particles with simple mixing rules that assume there are no organic-inorganic interactions in solution droplets (e.g. the ZSR approximation).

- In addition, a number of deliquescence scans were conducted during the Agnes Water campaign and one of these is presented in chapter 4. It shows 32 nm particles that exhibited a clear deliquescence transition at ~80% RH, resulting in their identification as predominantly ammonium sulphate particles. Only 4 studies have investigated the hygroscopic growth of marine aerosol particles as a function of RH and clear phase transitions were only observed in 2 of these (Berg et al., 1998; Fletcher et al., 2007). Therefore, this observation is an interesting contribution to the literature.

7.2.3 VH-TDMA development: Chapter 5

- Volcanic sulphate emissions from Iceland were detected at Mace Head Atmospheric Research Station on a day (26 June 2007) when the VH-TDMA was operated in parallel with an aerosol mass spectrometer (AMS). This provided an excellent opportunity to test the ability of the VH-TDMA to infer particle chemical composition based on comparison between scans of ambient particles with those of laboratory-generated particles of known composition. The VH-TDMA and AMS agreed that sulphuric acid comprised a significant fraction of the sulphate particle mass detected on June 26. However, the ammonium-to-sulphate molar ratio calculated from the VH-TDMA data (~1.1) was higher than corresponding ratio calculated from the AMS data (~0.45). This discrepancy could be explained by size-dependent neutralisation. The AMS measured sub-micrometre particles (d_p ~40–1000 nm) while the VH-TDMA only examined 50 nm particles. A number of laboratory and field studies have previously shown that for ammonia-limited environments (e.g. remote marine environments) the degree of sulphate particle neutralisation increases with decreasing particle size (e.g. Biskos et al., 2009; Fletcher et al., 2007). Thus, it is reasonable to expect that the VH-TDMA would measure a higher ammonium-to-sulphate molar ratio for 50 nm particles than the AMS measures for sub-micrometre particles. Therefore, the agreement between the VH-TDMA and AMS can be considered to be very good; both instruments detected pure sulphuric acid in volcanic particles and differences in the exact degree of neutralisation could be explained by the difference in operating size range. This was an important verification of the VH-TMDA's ability to identify ammoniated sulphate particles and it validates the conclusions drawn in the other chapters of this thesis.

7.2.4 Accumulation mode sea spray aerosol (SSA) particles: Chapter 6

- A bubble chamber was built at QUT and used to generate SSA particles from samples of seawater collected in Moreton Bay. Inspiration for these experiments was drawn from similar measurements conducted during the Mace Head campaign. The number size distribution of SSA particles produced in the chamber contained a dominant accumulation mode centred around 80 nm. This is consistent with recent field measurements (and other bubble chamber studies) which suggests that the aerosol production in the chamber was broadly representative of oceanic production.

- An original method was devised to calculate the organic fraction of chamber-generated accumulation mode SSA particles. The method was based on comparison of VH-TDMA scans of natural SSA particles and artificial SSA particles (which were generated from sea salt solutions prepared with ultra-pure deionised water). It was found that natural SSA particles were more volatile and less hygroscopic than the artificial SSA particles. This was almost certainly because they contained a seawater-derived organic component that wasn't present in the artificial particles. Thus, the seawater-derived organic fraction of natural SSA could be quantified by the average difference between the natural and artificial SSA volatility curves. Calculations were then made under the ZSR approximation to check whether the volatility-derived organic fraction was consistent with simultaneously measured hygroscopic growth factors. Excellent agreement was obtained, which validated the SSA organic fraction measurement.

- The new experimental method has several key advantages over previously used filter-based approaches for investigating the size-resolved composition of sea spray aerosol. The filter-based approaches (e.g. Keene et al., 2007a; Facchini et al., 2008b) require large concentrations of particles maintained over very long time periods (> 10 hrs) in order to collect enough SSA mass for accurate offline chemical analysis. Even then the chemical characterisation of accumulation mode SSA particles is still subject to significant uncertainties due to the small amounts of matter involved. In contrast, the VH-TDMA is an online number-based method, which means that only small concentrations of SSA (~100 cm^{-3}) are required for accurate analysis and these only need to be maintained for the time taken to complete a full VH-TDMA volatility scan, ~1–2 hrs. The result of this is that only small-scale bubble chambers and small samples of seawater are required, reducing the chances of contamination. The greater time resolution of the VH-TDMA method also allows investigation of the change in SSA composition over time.

- Accumulation mode SSA particles generated from Moreton Bay seawater samples in the QUT bubble chamber contained only a minor proportion of organics. The organic volume fraction of 71–77 nm diameter particles was only 8±6%. This fraction did not vary significantly with particle diameter in the range 38–173 nm or with water flow rate in the bubble chamber. This result is more than an order of magnitude below previous measurements of the organic fraction of accumulation mode SSA particles (Keene et al., 2007a; Facchini et al., 2008b). The reasons for this discrepancy are not yet clear but they may be related to the organic composition (coastal vs. open ocean; allochthonous vs. autochthonous) of the seawater samples. Further independent, size-resolved measurements of SSA produced from a variety of different seawaters are required to resolve this issue. This is important because the organic fraction of SSA will determine its water uptake properties and therefore its direct and indirect effects on climate.

7.3 Future studies

It must be said that our knowledge of the formation, composition and water uptake properties of marine aerosols is still incongruous with the scale of their coverage over the Earth's surface. This makes them deserving of much more scientific attention. Future studies should pay more attention to the link aerosols form between the oceans and the atmosphere. This works both ways. Marine aerosol properties are determined to some extent by what is happening physically, chemically and biologically in the waters below them. On the other hand, oceanic processes can be affected by aerosol-driven atmospheric phenomena. This interconnection has probably best been represented in its totality by the CLAW hypothesis (Charlson et al., 1987). However, there are many other important links between marine aerosols and the oceans and these should be kept in mind by future researchers. This can be achieved in projects that involve close collaboration between aerosol scientists and oceanographers.

There are two topics in the field of marine aerosol research that I feel are particularly worthy of further investigation; sea spray aerosols and reef-related particle nucleation.

Sea spray aerosols

Future research in this area needs to better link the chemical composition of aerosol particles to the nature of the seawater from which they're generated. This is especially important for the smallest but most numerous sub-micrometre sea spray particles whose chemical properties are still uncertain, as highlighted by chapter 6 of this thesis. Ultimately, more comprehensive efforts are required which link both aerosol production and composition with meteorological conditions, wave characteristics, bubble properties, marine biogeochemical processes and the physical properties of ocean water. All future studies, whether direct or broad, need to be conducted in a greater range of oceanic and coastal regions in order to fully capture the easily underestimated diversity of marine ecosystems. Finally, refined parameterisations must be developed so that state-of-the-art observations are utilised to their full potential in climate and air quality models.

Reef-related particle nucleation

Observations from Agnes Water suggest that the Great Barrier Reef (GBR) is a major source of secondary particles, but further measurements are required to confirm this. These measurements need to determine the spatial scale of GBR particle production, the frequency with which it occurs, the meteorological and tidal conditions that are conducive to event occurrence and the physicochemical characteristics of freshly nucleated particles over time. Particular attention should be paid to elucidating the mechanism behind reef-related nucleation events. The GBR is known to emit large amounts of dimethylsulphide (DMS), a well known particle precursor. However, the timescale between DMS emission and resulting particle formation, ~1–2 days, is too long for DMS to explain the GBR nucleation event described in chapter 3. Therefore, it is likely that other substances were also involved and determining these should be a focus of future studies. The implications of these questions are more than academic. Particles produced in GBR nucleation events appear to grow very quickly to sizes where they can participate in the direct and indirect effects of aerosols on climate. This means they may have an important influence on the climatic conditions (e.g. rainfall patterns) of North-Eastern Australia.