

A dedicated study of New Particle Formation and Fate in the Coastal Environment (PARFORCE): Overview of objectives and achievements

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[1] A dedicated study into the formation of new particles, New Particle Formation and Fate in the Coastal Environment (PARFORCE), was conducted over a period from 1998 to 1999 at the Mace Head Atmospheric Research Station on the western coast of Ireland. Continuous measurements of new particle formation were taken over the 2-year period while two intensive field campaigns were also conducted, one in September 1998 and the other in June 1999. New particle events were observed on ~90% of days and occurred throughout the year and in all air mass types. These events lasted for, typically, a few hours, with some events lasting more than 8 hours, and occurred during daylight hours coinciding with the occurrence of low tide and exposed shorelines. During these events, peak aerosol concentrations often exceeded 10^6 cm^{-3} under clean air conditions, while measured formation rates of detectable particle sizes (i.e., $d > 3 \text{ nm}$) were of the order of $10^4\text{--}10^5 \text{ cm}^{-3} \text{ s}^{-1}$. Nucleation rates of new particles were estimated to be, at least, of the order of $10^5\text{--}10^6 \text{ cm}^{-3} \text{ s}^{-1}$ and occurred for sulphuric acid concentrations above $2 \times 10^6 \text{ molecules cm}^{-3}$; however, no correlation existed between peak sulphuric acid concentrations, low tide occurrence, or nucleation events. Ternary nucleation theory of the $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ system predicts that nucleation rates far in excess of $10^6 \text{ cm}^{-3} \text{ s}^{-1}$ can readily occur for the given sulphuric acid concentrations; however, aerosol growth modeling studies predict that there is insufficient sulphuric acid to grow new particles (of ~1 nm in size) into detectable sizes of 3 nm. Hygroscopic growth factor analysis of recently formed 8-nm particles illustrate that these particles must comprise some species significantly less soluble than sulphate aerosol. The nucleation-mode hygroscopic data, combined with the lack of detectable VOC emissions from coastal biota, the strong emission of biogenic halocarbon species, and the fingerprinting of iodine in recently formed (7 nm) particles suggest that the most likely species resulting in the growth of new particles to detectable sizes is an iodine oxide as suggested by previous laboratory experiments. It remains an open question whether nucleation is driven by self nucleation of iodine species, a halocarbon derivative, or whether first, stable clusters are formed through ternary nucleation of sulphuric acid, ammonia, and water vapor, followed by condensation growth into detectable sizes by condensation of iodine species. Airborne measurements confirm that nucleation occurs all along the coastline and that the coastal biogenic aerosol plume can extend many hundreds of kilometers away from the source. During the evolution of the coastal plume, particle growth is observed up to radiatively

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active sizes of 100 nm. Modeling studies of the yield of cloud-condensation nuclei suggest that the cloud condensation nuclei population can increase by $\sim 100\%$. Given that the production of new particles from coastal biogenic sources occurs at least all along the western coast of Europe, and possibly many other coastlines, it is suggested that coastal aerosols contribute significantly to the natural background aerosol population. INDEX

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1. Introduction

[2] The relevance of natural particle formation relates to the significant contribution of aerosols to the Earth's radiative budget, and consequently, climate change. In terms of aerosol effects on climate, the role of aerosols comprises the greatest uncertainty [Penner et al., 1994; Houghton et al., 1995]. Aerosols contribute to the radiative budget through direct scattering of incoming solar radiation [Charlson et al., 1992; Russell et al., 1999; Charlson et al., 1999] and indirectly through determination of cloud physical and radiative properties [Twomey, 1974, Charlson et al., 1987]. With the increased emissions of anthropogenic aerosols and their precursors, the contribution of anthropogenic aerosols to global cooling and global warming has undergone substantial investigations; however, the results so far contain error bars of greater magnitude than the absolute forcing predicted [Houghton et al., 1995; Haywood and Boucher, 2000].

[3] Not only are there difficulties associated with predicting the highly nonlinear aerosol-cloud interactions [O'Dowd et al., 1999b, 1999c] and direct scattering efficiencies of complex aerosol mixes [Haywood and Shine, 1997], there are also difficulties and uncertainties associated with identifying and quantifying the impact of different source regions and the relative importance of natural and anthropogenic aerosols to climate forcing. In order to accurately understand the effect of anthropogenic aerosols on climate forcing, one must also quantify and understand the natural background production rate of atmospheric aerosols.

[4] A few locations have been identified as possibly important boundary layer sources of natural biogenic aerosols [Weber et al., 1998; Kavouras et al., 1998; Clarke et al., 1998]: the most obvious are over forests [Mäkelä et al., 1997; Kulmala et al., 2001], where biogenic VOC emissions are high, and around coastal regions during exposure of shore biota directly to the atmosphere during low-tide conditions [O'Dowd et al., 1998, 1999a]. Coastal nucleation events probably occur in most coastal environments. This is certainly true, at least, in western Europe, with frequent observations of particle production events being observed around the Scottish, Irish, English, and French coastlines [Aitken, 1897, 1911; Paugam, 1975; Jennings, 1995; O'Dowd et al., 1996]. Furthermore, coastal nucleation has been observed in the Southern Hemisphere around the Antarctic coastline [O'Dowd et al., 1997] and in the Tasmania coastal region [Bigg and Turvey, 1978].

[5] Investigations into elevated particle concentrations in the coastal environment began in the 1890s when John Aitken stumbled upon the phenomena of elevated particle concentrations in clean air around the coastline of King-

airloch, on the west coast of Scotland [Aitken, 1897]. At this location, Aitken noticed that when the wind was northwesterly and the sky clouded, particle concentrations were quite low ($200\text{--}300\text{ cm}^{-3}$), while if the wind was from the northwest and accompanied by sunshine, then the concentration often exceeded $10,000\text{ cm}^{-3}$. Through investigations with his mobile dust counter, or condensation nucleus (CN) counter, Aitken was able to rule out nearby sulphur springs as the source of these particles and for the next 10 or so years, the abnormal dust readings remained a mystery. In later writings, Aitken [1911] reported stumbling over more abnormally high readings at Appin, again on the west coast of Scotland. He noticed that at Appin, high readings of particle concentration occurred under similar conditions to the events observed at Kingairloch. He also noted that these high concentrations were not accompanied by a reduction in visibility, suggesting either that the plumes were so thin so as not to have any transparency effects, or the particles were so small that they did not effectively scatter sunshine. In the studies at Appin, concentrations of the order of $150,000\text{ cm}^{-3}$ were detected. These fascinating findings led Aitken to undergo a series of laboratory experiments in the search for the precursor vapor of these new particles. In these experiments, he studied the production of particles from hydrochloric acid, salt, and iodine and the influence of oxidising agents such as hydrogen peroxide and ozone on possible nucleation mechanisms. Although these experiments did not lead to any conclusive formation mechanism leading to the production of coastal new particles, there was evidence for particle production when iodine vapor was introduced into the system. Interestingly, Aitken concluded his study with an apology [Aitken, 1911, pp. 497–498].

I feel that an apology is due for presenting this paper. The subject is an uninteresting one to most people, and I have to admit that its presentation is badly focused and gives but a hazy impression. If it had not been for the discovery of the origin of the sun-formed nuclei at Kingairloch, the work would not have been done. Perhaps the difficulty of experimenting on a subject in such extremely small quantities of matter that produce such marked effects, and the varied nature of the contents of the paper may be some excuse for these effects.

[6] The coastal aerosol production phenomena observed by Aitken on the Scottish coast was also observed on the west coast of Ireland by Pollak and Murphy [1952]. Pollak and Murphy deployed a Nolan Pollak condensation counter in a mobile van laboratory donated by the brewing firm Arthur Guinness, Son and Co. This mobile unit was used to measure the spatial distribution of CN in Dublin and across the country during two transects covering more than

2000 kms. One of the main findings in these studies was the rapid increase in particle concentration to $\sim 200,000 \text{ cm}^{-3}$ as they approached the west coast of Ireland. Further studies into biogenic production of particles were conducted by *O'Connor* [1963]. While these studies produced useful findings, the actual nucleation mechanism leading to the production of new particles in the littoral zone was not elucidated.

[7] More recent studies by *McGovern et al.* [1996] reported regular occurrences of elevated condensation nuclei concentrations at the Mace Head Atmospheric Research Station and found these events occurred under conditions of solar radiation and elevated ozone concentrations. A later statistical study of CN concentrations at Mace Head found that the periods of elevated concentrations occurred both in clean and polluted air [*McGovern*, 1999]. *O'Brien et al.* [2000] conducted a neural network analysis of particle production events also; however, it should be noted that the analysis was conducted on total particle concentration at sizes larger than 10 nm, and consequently, most of the particle production events could not be included in their analysis. Their results indicated that tidal occurrence were not always necessary for particle production and most events occurred in polluted air.

[8] More comprehensive studies of the coastal nucleation phenomena were reported by *O'Dowd et al.* [1998, 1999a] and *Grenfell et al.* [1999]. In these studies, they concluded that new particle bursts were observed on most days during two intensive monthlong field campaigns and that, more often than not, these events were linked to shore exposure during low tide conditions and solar radiation. Typical concentrations encountered were $>200,000 \text{ cm}^{-3}$ with the majority of these particles occurring at sizes of between 3 and 10 nm. It should be noted that in the aforementioned studies, the particle counters regularly reached their saturation concentration of $180,000 \text{ cm}^{-3}$ and that this saturation concentration corresponds to real concentrations of in excess of $1,000,000 \text{ cm}^{-3}$ [*Hämeri et al.*, 2002]. *O'Dowd et al.* [1999a] concluded, using parallel measurements of OH and SO_2 , that these events were photochemically driven and that binary nucleation of sulphuric acid could be ruled out as a likely cause. They also found that predicted sulphuric acid concentrations could participate in ternary nucleation with water and ammonia; however, while this mechanism could produce enough new particles at undetectable sizes of 1 nm, there was insufficient sulphuric acid to grow these new embryos to detectable sizes of 3 nm. Consequently, *O'Dowd et al.* [1999a] concluded that a fourth species was required to condense on these new stable embryos and that this species could, plausibly, also participate in the nucleation processes. More recently, *O'Dowd* [2001] reported that the new particles could grow rapidly (over 8 hours) into accumulation mode sizes, even at Mace Head. This observed growth occurred in slack airflow during which it is thought that biogenic emissions can accumulate more readily and these events do not necessarily require the occurrence of low tide. Additionally, *O'Dowd* [2001] illustrated that the growth into radiatively active sizes ($>100 \text{ nm}$) leads to a 300% increase in both scattering coefficients and cloud condensation nuclei concentrations.

[9] Because of the frequency of nucleation events observed at Mace Head, this station became the focus for a dedicated pan-European nucleation study in the form of

New Particle Formation and Fate in the Coastal Environment (PARFORCE). During two intensive field campaigns, these nucleation events were studied in detail, using the best available techniques, to study the concentration of likely aerosol precursors, aerosol concentration, size and chemical properties. This paper summarizes the objectives and achievements of the PARFORCE project and provides an overview of the main results.

[10] It should be noted that while there has been considerable advances in measurement technologies, approximately 100 years on from Aitken's studies, the same difficulties arise, namely, such an extremely small quantity of matter is still very difficult to measure and quantify. Despite improved instrumentation, the measurement of the size and chemical composition of new aerosol particles is still not possible. Consequently, and despite Aitken's claims that this subject is uninteresting to most people, this subject is still of great interest with many open questions remaining and further progress to be achieved, not only on coastal nucleation, but on natural atmospheric aerosol nucleation processes in general.

2. Objectives

[11] The objectives of the PARFORCE investigation were to elucidate and understand the processes and conditions which promote and control homogeneous heteromolecular nucleation in the coastal boundary layer. In particular the objectives were to (1) determine the conditions and the rates under which homogeneous heteromolecular nucleation occurs in the coastal boundary layer, taking account of preexisting aerosol condensation sinks, precursor gas concentration, and microscale and macroscale meteorology; (2) examine whether these nucleation events can be explained by binary or ternary heteromolecular nucleation of inorganic acids and bases with water, or whether alternative nucleation schemes are likely to explain the observed events (i.e., organic embryo formation followed by organic and/or sulphate growth); (3) examine the influence of anthropogenic/continental air parcel mixing on coastal nucleation; (4) explore the growth rates of newly-formed particles; and (5) examine the long-term frequency of occurrence of coastal nucleation bursts and their duration. The methodology used to address the above objectives can be best broken down into the work packages listed in Table 1.

3. Experiment

[12] PARFORCE was conducted at the Mace Head Atmospheric Research Station located on the western coastline of Ireland ($53^{\circ}20'N$, $09^{\circ}54'W$). The research facility comprises three west-facing laboratory buildings, two approximately 50–100 m from the tidal zone and one approximately 300 m in from the coastline. Between the shore laboratories stands a 22-m tower with a 10-m tower located on the north-facing gable end of the more northerly shore laboratory. The coastal zone around the west coast of Ireland is quite inhomogeneous [*O'Dowd et al.*, 2002] with Mace Head located on a peninsula almost totally surrounded by coastline, and consequently, tidal zones (see Figure 1). The location of the monitoring station and the peninsular nature of Mace Head itself provides a unique opportunity to study particle formation events at different distances from

Table 1. List of Work Packages and Activities Conducted Under PARFORCE

Work Package	Activity
1	examine the microscale factors which influence new particle formation in the coastal environment fast response measurements of gas-phase aerosol precursors and oxidant fast response measurements of the complete aerosol size distribution and condensation sinks fast response aerosol nucleation/source rates fast response micrometeorology to examine turbulent fluctuations
2	examine the macroscale conditions which promote nucleation events vertical profiles of meteorological parameters lidar measurements of boundary layer structure, evolution, and large-scale mixing
3	examine the composition of new particles using indirect methods examine nanometric aerosol growth factors to infer chemical composition examine the condensed organic and inorganic aerosol composition to identify primary aerosol species, particularly organic aerosol which may have been involved in nucleation events
4	develop theoretical models in close conjunction with the experimental results in order to put marine aerosol nucleation into a more realistic and robust theoretical framework; modeling phase transitions the study of homogeneous heteromolecular nucleation of the most relevant species in the atmosphere by using a model based on the recently developed ternary nucleation theory the study of phase transitions and mass transport between phases by using a Lagrangian parcel model with multicomponent condensation and detailed aqueous-phase chemistry models
5	examine the spatial scales over which coastal nucleation occurs determine the near-surface nucleation gradient conduct spatial mapping experiments of production regions
6	conduct long-term measurements of nucleation events to consider temporal context
7	examine the growth rates and evolution of newly formed nanometric aerosol through measurement and modeling studies
8	data validation guidelines, detailed data management, central database management, coordination of case studies and analysis, data distribution, assembling data formats for modeling case studies, and ensuring the smooth flow of data between the modeling and experimental activities

the tidal source region depending on recent air parcel trajectories. This midlatitude station is subject to prevailing westerly winds associated with the easterly tracking cyclonic systems of the North Atlantic. Typically, marine air encountered at Mace Head is considered to be representative of background North Atlantic marine air. Two intensive field campaigns were conducted, one in September 1998 and the second in June 1999. Along with intensive field campaigns, continuous measurements of new particle formation were also undertaken over the 2-year period.

[13] A detailed suite of aerosol, gas and meteorological instrumentation was deployed during the intensive field campaigns. Total aerosol concentrations were measured at sizes larger than 3, 5, and 10 nm using condensation particle

counters (CPCs). Aerosol size distributions were taken with Differential Mobility Particle Sizers covering the size range from 3 up to 1000 nm [O'Dowd *et al.*, 2002]. Supermicron size distributions, from 0.5 up to 300 μm , were taken using Particle Measurement Systems FSSP and OPA optical particle counters. Aerosol chemical concentration was determined from ion chromatography on impactor samples, single particle analysis on Transmission Electron Microscope samples [Mäkelä *et al.*, 2002], and hygroscopic growth using an ultrafine tandem differential mobility analyser (TDMA) [Väkevä *et al.*, 2002].

[14] A range of gas phase species, relevant to aerosol formation, were measured in parallel to the aerosol meas-

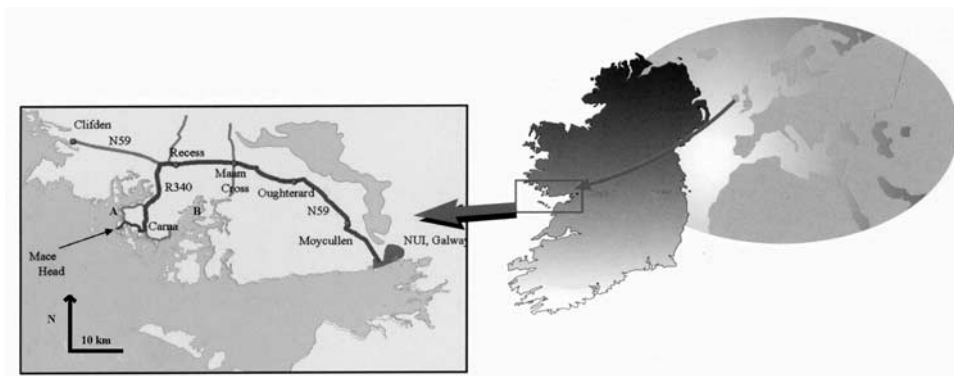


Figure 1. Location of Mace Head on the west coast of Ireland.

urements. These covered species such as NH_3 , SO_2 , H_2SO_4 , OH, methane sulphonic acid (MSA), O_3 , IO, VOCs ($\text{C}_8\text{-C}_{16}$) [Sartin *et al.*, 2002], and various halocarbons (CH_3Br , CH_3I , CH_2ClI , CH_2I_2 , CHBr_2I) [Carpenter *et al.*, 1999; Carpenter and Liss, 2000]. Adjunct measurements of IO were taken for a limited period [e.g., Aliche *et al.*, 1999]. Hydrogen peroxide and organic peroxides were also measured during both campaigns [Morgan and Jackson, 2002].

[15] Standard meteorological measurements (wind speed, wind direction, relative humidity, air temperature, and total and ultraviolet solar radiation) were available as standard parameters at Mace Head. Additional micrometeorological measurements were also conducted at the shore lab from 3 and 20 m. The micrometeorological measurements comprised fast response (3-D) wind field and temperature and water vapor fluxes were also measured. From this package, vertical fluxes of heat, water vapor and momentum were acquired along with drag coefficient and wind stress. A detailed characterization of the local micrometeorology and fluxes is discussed by De Leeuw *et al.* [2002]. Boundary layer structure was determined using a Lidar (Light Detection And Ranging) system and by in situ measurements using an aircraft. A full report on boundary layer structure measurements is given by Kunz *et al.* [2002]. $\text{JO}^{(1)\text{D}}$ measurements were obtained using a high-resolution filtered radiometer to provide a measure of photochemical activity. Tidal amplitude was calculated using a standard tide prediction software package for the area and, during the second (June) campaign, water column pressure was measured to give tide amplitude variation.

[16] The first intensive field campaign was conducted in September 1998 from Julian Day (JD) 250 (7 September) to JD 274 (31 October) while the second campaign was conducted in June 1999 from JD 154 (3 June) to JD 182 (1 July). During the September campaign, all air sampled was either of marine or polar origin except for one polluted period from JD 262–265. The June campaign similarly was dominated by marine or polar maritime air masses except for JD 174–176, which was dominated by polluted European air. During the June 1999 campaign, two research flights were conducted, one to examine the spatial scale of the observed nucleation events and the other to examine the growth and evolution of the new particle mode as the coastal plume advected away from the coastal source regions [O'Dowd, 2002].

4. Results

4.1. Aerosol Characteristics

[17] Aerosols and gas phase characteristics associated with nucleation events are discussed in detail in an associated paper [O'Dowd *et al.*, 2002]. In that study, events are classified into four types: Type I events occurred under clean marine westerly flow and when air trajectories passed over the shore region approximately 100 m upwind (west) of the Mace Head laboratory; Type II events occurred when clean marine air had advected over multiple shore regions about 10–20 km upwind (northwest) as well as over the foreshore in front of the laboratory; Type III events occurred under polluted conditions when air had advected over shore regions about 1–3 km to the southeast and east of the station; and Type IV were null events due to air arriving

from the northeast to the laboratory, not having advected over shore regions. It should be noted that although Type IV events were classified as null events at Mace Head, deployment of a remote CPC on a small island adjacent to Mace Head (i.e., connected during the low tide period and separated during high tide) indicated that after the air had advected past the station and over the shore at Mace Head, nucleation was again observed [Hämeri *et al.*, 2002].

[18] Figure 2 illustrates a contour plot of the occurrence of new particle events over a period of 3 months [O'Dowd *et al.*, 2002]. It is clearly seen that these coastal events occur during periods of solar radiation which overlap with low tide conditions. An example of a typical Type II event occurring around low tide and in the late morning is shown in Figure 3. Background particle concentrations were of the order of $300\text{--}400\text{ cm}^{-3}$ throughout the morning and toward the period of the low water mark. As the tide receded almost to its low water point, particle concentrations rapidly increased to 10^6 cm^{-3} and the duration of this event lasted almost 5 hours. The mean duration of events during both campaigns was ~ 4.5 hours while the longest events lasted up to 8–9 hours. While the event shown here illustrates the occurrence of particle production near midday, it should be noted that the events generally track the low-water mark rather than peak solar radiation. Consequently, when two low-tide cycles occur during daylight hours, two nucleation events will occur [O'Dowd *et al.*, 2002]. It should be noted that biogenic vapors are continuously emitted from the coastal environment, but are greatly enhanced during the low tide period. If the emissions are sufficient, or if their concentrations can accumulate under stagnant wind conditions, nucleation events may also occur [e.g., O'Dowd, 2001].

[19] Also shown in Figure 3 is the $\text{O}^{(1)\text{D}}$ production rate along with the concentration of sulphuric acid. The photolysis rate indicates low cloud cover and a typical diurnal cycle. Similarly, sulphuric acid follows closely the photolysis rate, also illustrating a clear diurnal cycle which was observed throughout the campaign. The nucleation event is not correlated to the peak sulphuric acid concentration and actually precedes this peak by about an hour or so. In general, sulphuric acid peak concentration was not correlated with the production of new particles. In this case, however, it can be noted that as the particle production starts, the sulphuric acid concentration had started to rise with $\text{JO}^{(1)\text{D}}$, and as production gets stronger, there is a sudden reduction in sulphuric acid concentration. A short time later, as the production rate of particles decreases, the acid concentration starts to increase again up to its maximum value. During the start of the event, sulphuric acid concentration was $\sim 2 \times 10^6\text{ molecules cm}^{-3}$, compared to its peak value after the event of $8 \times 10^6\text{ molecules cm}^{-3}$. In general, the durations of the events were found to increase as tidal amplitude increased, and consequently, more biota was exposed to the atmosphere over the foreshore.

[20] Generalised size distributions encountered during clean and polluted (continental) background and event conditions are shown in Figure 4. The background marine submicron size distribution was typically bimodal with a fine mode at 30–40 nm and an accumulation mode at 150–200 nm. By comparison, continental air contained a monomodal size distribution at approximately 100 nm. The

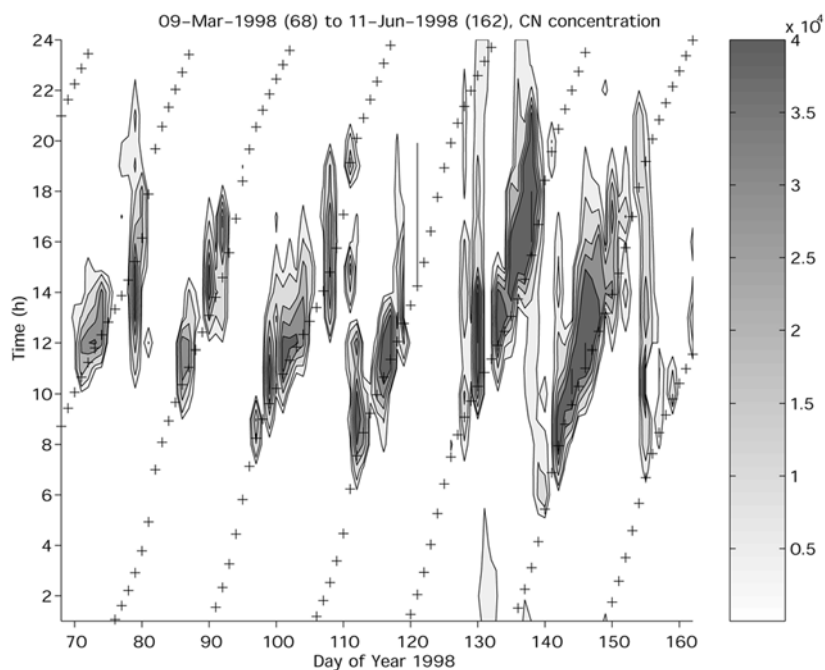


Figure 2. Total particle concentration over a 3-month period at Mace Head. Low tide is marked with a cross. Units of color scale are cm^{-3} . Particle concentrations are 1-hour averages.

nucleation mode was found to vary significantly depending on event type. During the September campaign, the Type I nucleation mode was found to have a peak at about 3 nm with associated concentrations of $>10^4 \text{ cm}^{-3}$. Type II events possessed a nucleation mode at sizes around 5–6 nm and concentrations generally $>10^5 \text{ cm}^{-3}$. This difference between Type I and II events, both occurring in clean marine air, is attributed to greater growth times associated with Type II events as the air had advected over source regions more than 10 km up wind (along with the local particle production at Mace Head), while Type I events typically had shorter growth periods corresponding to advecting over 100-m length scales. Type III events generally possessed a mode radius nearer to 10 nm due to the

distance of 2–4 km from the source region and associated advection time, but lacking more local production of particles. Differences between Type I and II cases were less obvious during the June campaign since the events were considerably stronger compared to the Autumn cases, and the local production was so much more intense. Type I nucleation mode spectra typically possessed a mode radius of 5 nm and concentrations, at times, exceeding 10^6 cm^{-3} . A stronger aerosol production period during the June campaign compared to the September campaign is borne out by statistical analysis of the nucleation mode and preexisting aerosol concentrations during events in both clean and polluted air [O'Dowd *et al.*, 2002]: The nucleation mode concentrations during the Summer campaign are,

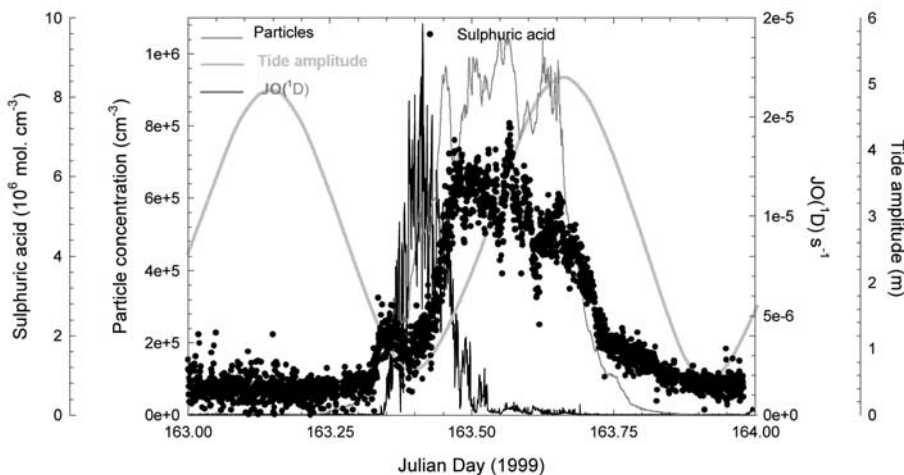


Figure 3. Variation in total particle concentration, sulphuric acid, $\text{JO}(^1\text{D})$, and tidal amplitude during a typical coastal nucleation event observed at Mace Head.

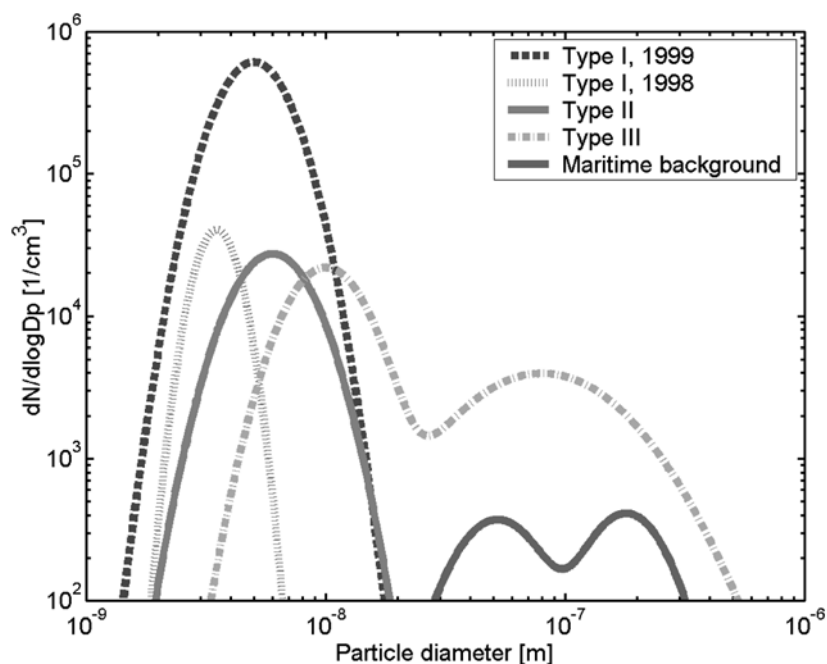


Figure 4. Idealized size distributions for different event types derived from spectral measurements.

on average, three times greater than that occurring in Autumn campaign, regardless of clean or polluted air masses. This higher average nucleation mode concentration during bursts in Summer may be due to enhanced biological emission and photochemical activity during Summer compared to Autumn.

4.2. Sulphuric Acid, MSA, and OH

[21] Figure 5 provides a statistical overview of the H_2SO_4 , MSA, and OH measurements during the June 1999 campaign. In general, H_2SO_4 levels correlated well with ambient OH concentrations. Both compounds showed diurnal cycles clearly driven by photochemistry and, including MSA, no correlation was observed with the tidal cycle. However, as discussed in detail by *Berresheim et al.* [2002], on occasion, fluctuations in sulphuric acid and MSA concentration and particle concentration were significantly anticorrelated; however, peak acid concentration was not correlated with particle production. As indicated in Figure 5, both compounds were still present at night with significant concentrations. With respect to H_2SO_4 , *Berresheim et al.* [2002] propose the presence of a nighttime source perhaps involving Criegee radical oxidation of SO_2 , and corresponding precursor reactions of ozone with unsaturated hydrocarbons. MSA diel cycles showed significant variations overlapping with its daytime photochemical production. It was found that MSA could evaporate from aerosol particles under drier conditions and that the MSA gas-particle partitioning equilibrium is very sensitive to ambient relative humidities. OH concentrations were significantly affected by (unknown) chemical reactions particular to the coastal marine boundary layer as suggested by comparison with OH values calculated from a photochemical box model [*Berresheim et al.*, 2002]. Also, correlations were found between OH and ultrafine particle concentrations during a particle nucleation event occurring at midday

on JD 168 (17 June). These results suggest a strong relationship between the atmospheric oxidation capacity and the particle nucleation potential in the coastal marine boundary layer.

4.3. Organic Gases

[22] Gas chromatograph-mass spectrometer (GC-MS) analysis of air samples taken at Mace Head revealed the presence of 16 volatile organic compounds (VOCs) in the range $\text{C}_8\text{-C}_{16}$. The VOCs observed consisted of 8 $\text{C}_9\text{-C}_{16}n$ -alkanes at concentrations in the range $<2\text{-}126$ pptv and 8 $\text{C}_8\text{-C}_{14}$ oxygenates ($<2\text{-}427$ pptv). There was no observed effect of tide height on the VOC concentrations. Temporal trends of the 12 compounds continuously quantified, by gas chromatograph-flame ionisation detector (GC-FID), during June 1999 [*Sartin et al.*, 2002] showed a nighttime maximum and early-afternoon minimum. This diurnal pattern was more prominent for the n -alkanes than for the oxygenated species. Both these generalised observations (diurnal variations in concentration; greater amplitude in diurnal variations for more reactive compounds) suggest that the daily variation in concentration of these VOCs is dominated by radical chemistry. During the nighttime period, when there is no photochemistry and thus no photochemically produced radicals, emissions from seawater and the relatively low marine boundary layer (MBL) act to produce a significant increase in ambient VOC concentrations. During the daytime, reactions with photochemically produced radicals initiate a reduction in ambient VOC concentrations.

[23] Analysis of coastal seawater samples taken at Mace Head showed mean concentrations of Σn -alkanes and Σ oxygenates to be $5.4 \mu\text{g L}^{-1}$ and $9.8 \mu\text{g L}^{-1}$, respectively. The observed n -alkane levels were ~ 10 times greater than previously published open-ocean concentrations [*Cripps*, 1992; *Eichmann et al.*, 1980]. The concentrations in coastal water were also found to be $\sim 10^3$ times greater than those

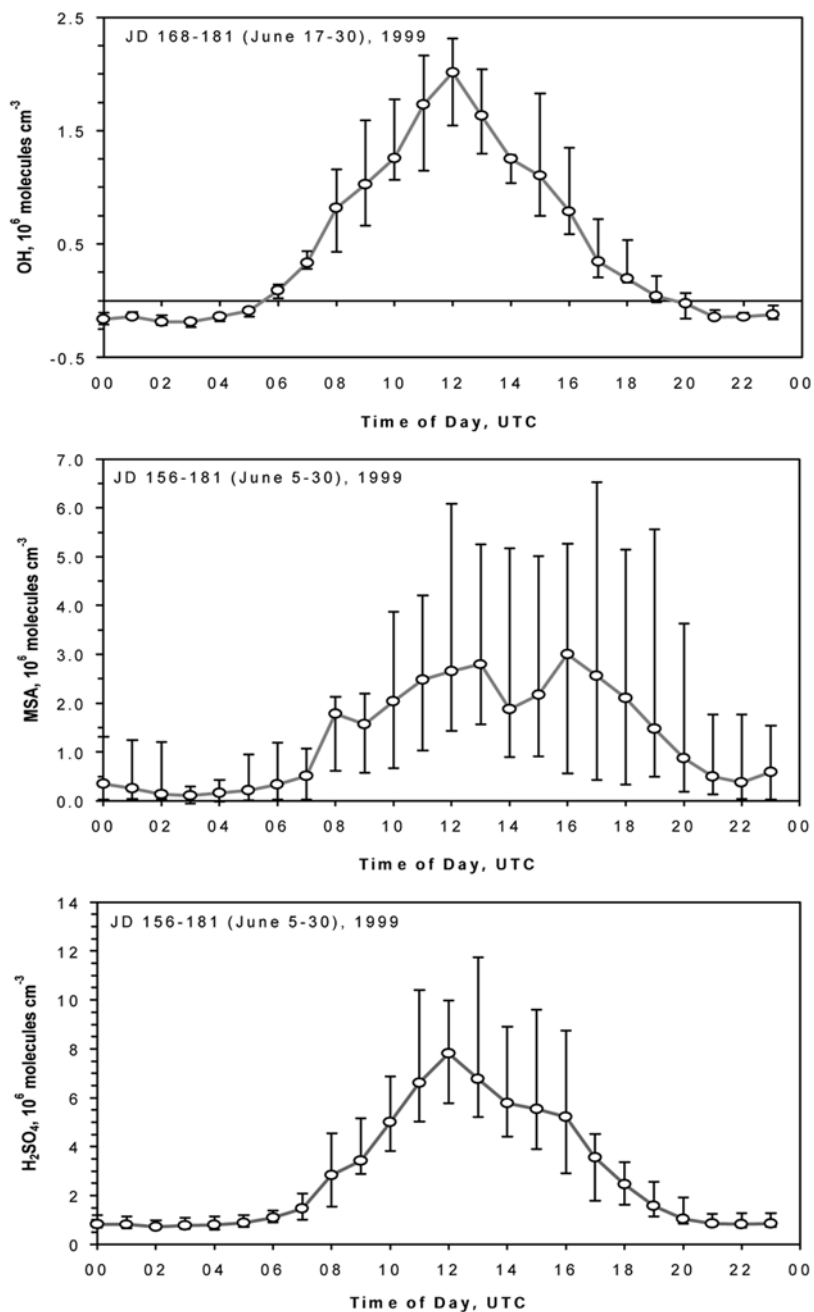


Figure 5. Composite hourly median concentrations (circles) and 25–75% quartile ranges (vertical bars) of OH, MSA, and H₂SO₄ measured during the June 1999 PARFORCE field campaign. Pollution episodes (JD 157 and JD 176) and low-frequency OH measurements are not included (for details see *Berresheim et al.* [2002]).

observed in the atmosphere and, therefore, suggest that there will be a release of these volatile compounds from the water surface to the atmosphere. The sea-to-air flux of VOCs was calculated using the VOC concentrations in seawater, wind speeds, and the expression from *Liss and Merlivat* [1986]. True maritime air arriving at Mace Head (Type I: as indicated by backward air mass trajectories) was found to have lower VOC concentrations than in air that travelled along the coast (Type II), consistent with lower VOC concentrations in open-ocean seawater. Published data were not available for the oxygenates.

[24] A simple Lagrangian box model of the atmosphere that included the calculated emissions from the ocean surface, MBL height, measured OH radical concentrations, and VOC-OH reaction rate constants overpredicted the observed amplitude in the diurnal variations of concentration. Specifically, the observed reductions in *n*-alkane concentrations in the morning could not be accounted for using OH chemistry alone. However, the reactions of VOCs with halogen radicals have been proposed as an efficient loss mechanism for reactive compounds in the MBL [*Singh et al.*, 1996]. The reactions of *n*-alkanes with bromine are too slow to

account for the observed concentration changes but an average chlorine concentration of 10^4 – 10^5 cm^{-3} would be sufficient to account for the observed reductions in concentrations in the morning. Chlorine concentrations of 10^4 – 10^5 cm^{-3} have been reported previously in the MBL [De Haan *et al.*, 1999; Spicer *et al.*, 1998].

[25] From the measurements made at Mace Head, it seems unlikely that the C_8 – C_{16} VOCs observed can account for the particle bursts that occur around low tide. No correlation between VOC concentration and tidal height was seen. However, it is possible that heavier, semivolatile organic compounds (SVOCs), not detected by the methods employed at Mace Head, may be emitted from the tidal zone (from biota, an organic film on sediments, and/or residue seawater) and either participate in nucleation and/or growth.

4.4. Peroxides and Ozone

[26] Hydrogen peroxide (H_2O_2), methyl hydroperoxide (CH_3OOH), hydroxymethyl hydroperoxide ($\text{CH}_2(\text{OH})\text{OOH}$), peroxyacetic acid ($\text{CH}_3\text{C}(\text{O})\text{OOH}$), and ethyl hydroperoxide ($\text{CH}_3\text{CH}_2\text{OOH}$) were detected during both campaigns [Morgan and Jackson, 2002]. Hydrogen peroxide and CH_3OOH were the only species observed at quantifiable levels in atmospheric samples. Hydrogen peroxide concentrations during September and June ranged from below the limit of detection to 1.53 and 7.1 ppbv with overall mean concentrations of 0.23 and 1.58 ppbv, respectively. Sampling in clean air in September showed a mean concentration of 0.33 ppbv compared to 0.14 ppbv from sampling in polluted air. The clean air and polluted mean concentrations for June were 1.75 and 0.725 ppbv, respectively. Comparisons of the two campaigns show that higher levels of H_2O_2 were recorded during June 1999. Although temperatures were lower during this period than September, solar radiation was significantly higher resulting in increased photochemical activity and the production of hydroperoxides as well as promotion of the emission of biogenic gases from marine biota. During rainfall events, gas phase concentrations of H_2O_2 and organic hydroperoxides (ROOHs) fell to below the limit of detection of the instrument (20 pptv) due to their high solubility. Analysis of eight rainfall samples recorded H_2O_2 concentrations in the range 3.1 to 7.7 $\mu\text{mol l}^{-1}$. Methyl hydroperoxide was not quantifiable in rainfall samples, but $\text{CH}_2(\text{OH})\text{OOH}$ was present in concentrations between 0.13 and 0.19 $\mu\text{mol l}^{-1}$.

[27] Higher concentrations of hydroperoxides were recorded during periods of maritime airflow. This can be attributed to the higher levels of NO_x present in polluted continental air, which scavenge free radicals necessary for peroxide production. The impact upon the H_2O_2 concentration during these polluted air periods was observed during both campaigns. During the clean air period from Julian Day 252 to Julian day 258 1998, H_2O_2 levels were generally higher than the rest of the September campaign. Back trajectories show that the source region of air reaching Mace Head during this period moved from the mid-Atlantic to an Arctic source region suggesting a change in the clean air composition, which favored an increase in CH_3OOH production but a reduction in H_2O_2 . During the polluted period of Julian Day 260 to Julian Day 269 1998 the concentration of H_2O_2 remained low and the average daily

H_2O_2 concentration exhibited no change as the air mass source region extended through Eastern Europe.

[28] Hydrogen peroxide exhibited a relationship with the tidal cycle at Mace Head with higher concentrations being observed for higher tidal amplitude and low tide occurrence. Both the tidal amplitude and time of maximum low tide affected the H_2O_2 trend during both campaigns. This feature was apparent on days experiencing maritime and modified maritime air that had passed over tidal regions upwind of Mace Head. Hydrogen peroxide concentrations appeared to be unrelated to meteorological parameters. The increase in concentration of H_2O_2 occurs generally at the same time as the nucleation events. A role for H_2O_2 in the coastal nucleation events has not yet been determined. With the data available, it is shown that H_2O_2 concentrations at Mace Head are affected by processes which occur during low tide. Biogenic emissions from exposed marine biota have to be investigated to determine the controlling factors on H_2O_2 concentration in this coastal environment. Ozone is measured continuously at Mace Head [e.g., Derwent *et al.*, 1998]; however, no tidal relationship was observed. While it was difficult to see any coherence with the occurrence of new particles, during one strong nucleation event (e.g., JD 163, 1999), a noticeable reduction in ozone was observed simultaneously with the production of particles.

4.5. Biogenic Halocarbon Measurements

[29] In the original work program, the role of biogenic halocarbons were not considered as being associated with the particle production events, and consequently, the bulk of the effort was devoted to sulphuric acid, OH, MSA, and VOC measurements along with SO_2 and ammonia. Nevertheless, there were limited adjunct measurements conducted [Carpenter and Liss, 2000] during the September campaign. Similarly, measurements of IO were conducted over the same period as halocarbon measurements [Carpenter *et al.*, 2001]. Since it was considered that the coastal biota, including seaweed, was the primary source of these biogenic halocarbons, a number of these species were examined for both VOC and halocarbon emissions using a dynamic gas exchanger system (cuvette technique) [Mäkelä *et al.*, 2002]. The striking observation was that no identifiable VOC emissions were detected; however, significant emissions of halocarbons were. In particular, *Fucus spiralis* was the strongest emitter of tribromomethane and diiodomethane, both very short-lived biogenic halocarbons. Emission rates for CH_2I_2 of 1.11 $\text{ng s}^{-1} \text{m}^{-2}$ were measured for *Fucus spiralis*, while 8.34 $\text{ng s}^{-1} \text{m}^{-2}$ of CHBr_3 was observed to be emitted in the same sample. *Fucus vesiculosus* was also observed to be a strong emitter of both species.

[30] In terms of tidal cycles, the only species that illustrated noticeable coherence with low tide were CH_2I_2 and CHBr_3 , measured with a mass spectrometer, and IO, measured with a long-path DOAS. Peak concentrations of CH_2I_2 measured during September were of the order of 0.25 ppt [Carpenter *et al.*, 2000], while peak IO concentrations of a few parts per thousand were observed during low tide [Carpenter *et al.*, 2001]. It should be noted that the DOAS measurements were taken over a 15-km path length over two tidal regions, each of the order of 100–200 m deep. Consequently, it is conceivable that concentrations in the

tidal zone could have been 1–2 orders of magnitude higher than the observed peak.

4.6. Aerosol Chemical Composition

[31] The bulk chemical composition of the total aerosol was largely determined by air mass origin, and, with the exception of sea salt aerosol generated in the surf zone, was not influenced by the state of the tide, as expected since the relative mass of the locally produced new particles is small. Oceanic phytoplankton productivity, using methanesulphonate as an indicator of biological activity, was significantly greater in June 1999, showing the occurrence of offshore algal blooms. This implies that methanesulphonate production from DMS oxidation was not simply a function of wind speed, which influences the rate of transfer of DMS across the ocean-atmosphere interface. MSA/non-sea-salt sulphate (NSSS) molar ratios reflect this increased productivity and show that production of MSA was high relative to NSSS in clean marine air during the June campaign, when lower ratios only occurred due to the presence of continental (anthropogenic) sulphates. Mean (\pm SD) and median ratios in clean air during 1998 (JD 253–259) and 1999 (JD 157–158, 170–173, 178–179) were 1.3 ± 1.2 and 0.9 (1998) and 35 ± 20 and 31 (1999), within the range of values previously reported [Allen *et al.*, 1997, and references therein]. Interestingly, rates of MSA production during both campaigns, but especially during 1998, increased during transition periods when cleaner air masses gave way to more polluted conditions, presumably due at least in part to increasing importance of the reaction of DMS with NO_3 , but tended to fall away later during pollution events as DMS was depleted. Advection of continental air masses during September 1998 (JD 263–270) was associated with very high concentrations of excess sulphate, as well as ammonium, and only during this period did nitrate reach levels around $10 \mu\text{g m}^{-3}$. Oxalate was also measured in the aerosol, and showed highest concentrations in polluted air with close correlation with anthropogenic sulphate and nitrate.

[32] The size-dependent chemistry was measured using Berner and MOUDI impactors during both campaigns, with samples collected either over periods of several days or integrated over several periods of daytime (or nighttime) low tide. Continuous size distributions were obtained from the raw data using the procedure described by Winklmayr *et al.* [1990] and modified for the inversion of size distribution data obtained using the MOUDI by Keywood *et al.* [1999]. The 50% cut-off parameters were adjusted according to the actual flow rates employed.

[33] Two impactor runs are illustrated in Figure 6, where the 1998 data were obtained during a polluted period (JD 267–269) and the 1999 data during a period of quite clean air (JD 157–164). In unpolluted marine air, most of both methanesulphonate and excess sulphate was present in 0.3–0.8 μm particles, while in polluted air both species were bimodal and present at similar concentration levels in 0.3–0.8 μm and 1–2 μm size ranges. Both chloride and nitrate possessed a large 1–2 μm mode in continental air; however in marine air most of the sea salt chloride was contained within particles of 2–20 μm , and the size distribution of nitrate was governed by surface area availability, resulting in a single broad mode with maximum at 2 μm .

4.7. Ultrafine Particle Composition

[34] The measurement of ultrafine or nucleation mode particle composition still poses one of the greatest difficulties to underpinning the primary processes leading to new particle formation and growth. While we cannot, at this stage of current technology, determine either the size or the composition of critical embryos, or actual new particles, we can try to measure the characteristics of nanometer-sized aerosol, and thereby understand more about the vapor precursors that lead to the growth of critical embryos into ultrafine particles if this vapor is different from the nucleating species. During PARFORCE, an ultrafine hygroscopic growth TDMA was deployed to examine the hygroscopic growth factors in recently formed particles [Väkevä *et al.*, 2002]. The principle of this measurement is that particles of a certain size and chemistry will undergo a specific increase in size after being subjected to a certain humidity field.

[35] Under clean conditions at Mace Head, 20-nm particles were observed to possess a hygroscopic growth factor typical of ammonium sulphate (1.4), while 8-nm particles often possessed a growth factor corresponding to a mostly nonsoluble aerosol species (1.05), suggesting that these particles are not composed of sulphate or common ionic soluble compounds typically found in atmospheric aerosols. It should be noted that if the particle production event continued through toward midday, the solubility, or hygroscopic growth factor was observed to increase in line with the production rate of sulphuric acid. An example of the growth factor of 8-nm particles increasing in line with sulphuric acid production is illustrated in Figure 7 for the event shown in Figure 3. This unusual result would generally point to an organic composition for the new particles; however, no link was found between VOCs and either emissions from the biota or low tide. Similar behavior could also be explained by a very insoluble inorganic aerosol composition, as iodine oxide (e.g., I_2O_4 has been found to be very insoluble in most solvents, including water [Ellestad *et al.*, 1981; Roman, 1933]).

[36] One direct method of chemically fingerprinting the primary species, other than sulphate, leading to the production of these new particles was Transmission Electron Microscopy and elemental analysis (EDX). The difficulty with such methods are in (1) getting enough new particles to locate a sufficient amount to analyze on a filter or stub and (2) separating the new particles from the relatively large preexisting particles. The method employed on PARFORCE was to electrically precipitate sub-10-nm particles onto a TEM stub, thus providing reasonably sharp partitioning between the new and preexisting aerosols [Mäkelä *et al.*, 2002]. The very low charging efficiency of nanometer particles was overcome by the extraordinary large concentrations encountered during coastal events, and sampling over 2–3 events of the order of 4–6 hours in duration. As a result of this set-up, sufficient particles were captured for further analysis. The analysis of particles as small as 6–7 nm resulted and almost all of these particles were observed to contain both sulphate and iodine, with some exceptions containing only iodine. It should be noted that no chloride or bromide was identified. While it is difficult to quantitatively state the relative concentration of iodine to sulphate, it was clear that these were the detectable compounds in the particles. In particles containing both sulphate

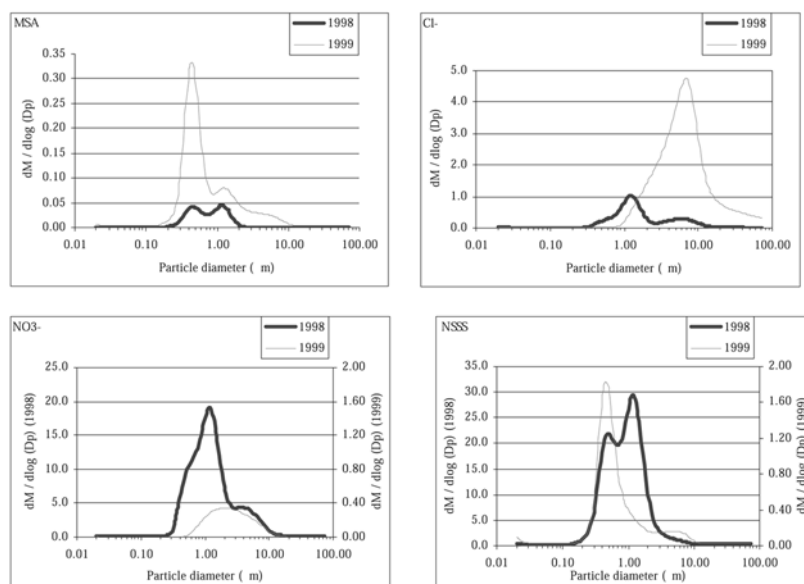


Figure 6. Size distributions of methanesulphonate, chloride, nitrate, and excess sulphate.

and iodine, the relative contribution appeared to be roughly similar. By contrast, the relative proportion of sulphate to iodine in 50- to 100-nm particles was significantly greater than in the nanometer particles. Taking these results into context with the TDMA results, there is strong evidence for iodine being one of the primary species producing detectable particles in this environment. The fact that sulphate was present in most of the particles can be explained by these samples having been taken coinciding with peak sulphuric acid production followed by enhanced condensation.

4.8. Meteorological Influence on Nucleation

[37] A Lidar system and a micrometeorological package were deployed to examine the effect of mixing and turbulence on nucleation events [Kunz *et al.*, 2002; de Leeuw *et al.*, 2002]. Lidar observations determined that the boundary layer was often multilayered in structure, and that these

layers, particularly the surface layer, could evolve rapidly. For example, the surface layer could evolve from 600 to 1300 m over a period as short as 2 hours; however, no effect on nucleation was observed. Measurements of heat, water vapor, and momentum fluxes were taken at heights of 3 and 22 m above the surface, as were vertical variances in wind fields. Because of the large range of conditions encountered, it was difficult to determine clear relationships with various meteorological parameters, low tide and nucleation events.

[38] In summary, no correlation was found between the probability of particle production and enhanced turbulence during low tide conditions; however, a positive correlation was found between kinematic heat flux and particle production probability, while a negative correlation was found with kinematic water vapor flux and relative humidity [de Leeuw *et al.*, 2002]. It is considered that as the water recedes during low tide, the shore area becomes drier, thus

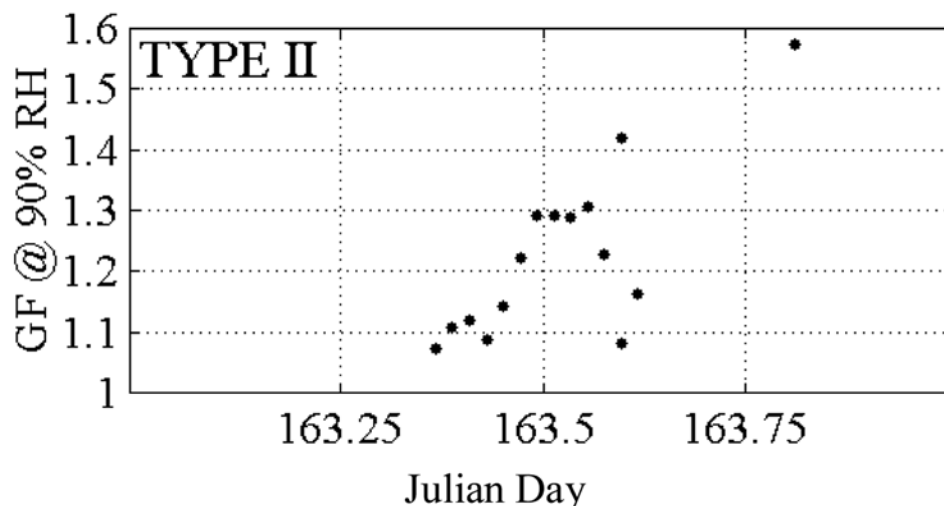


Figure 7. The 8-nm particle hygroscopic growth factor during a Type II coastal nucleation event.

reducing water vapor flux and increasing heat flux. These two factors may aid in the vertical transport of biogenic gases and/or the stressing of the biota which is known to increase halocarbon emissions.

4.9. Aerosol and Precursor Vapor Source Rates and New Particle Growth Rates

[39] Theoretical and analytical tools have to be used in conjunction with the experimental data to elucidate the processes leading to the observed nucleation phenomenon. In particular, these tools have to be used to estimate the nucleation rate of new particles since this and the precursor vapor source rates cannot be measured. In this study, to determine the required nucleation rates and vapor concentrations and source rates, we used a combination of recently developed ternary nucleation code for sulphuric acid, ammonia, and water to estimate nucleation rates; a new analytical technique which utilizes only size distribution data to estimate nucleation rates and vapor source rates; and a sectional aerosol dynamics model.

[40] Detectable-size particle source rates and growth rates are directly inferred from the rate of change of nucleation mode particles (between 3 and 10 nm) measured at the shore laboratory using the 1-Hz CPC data. From the CPC data, source rates of detectable, sub-10-nm particles were estimated to vary between $1\text{--}2 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ to a peak value of $6\text{--}7 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$. Since particles of at least 3 nm are detected after the air advects for 20–25 s from the source region, this implies a minimum growth rate of 0.1 nm s^{-1} from 1 to 3 nm. It should be noted that during the strongest events, growth up to 10 nm was observed also, leading to growth rates of 0.36 nm s^{-1} .

[41] *Dal Maso et al.* [2002], used the source rates of 3-nm particles, combined with the changes in the aerosol size distribution and accounting for the preexisting aerosol condensation sink, to estimate growth rates of $0.004\text{--}0.5 \text{ nm s}^{-1}$. In these calculations, the aerosol condensation sink varied from a general background value of approximately $2 \times 10^{-3} \text{ s}^{-1}$ to 5 s^{-1} during the most intense bursts with the dominant contribution coming from the nucleation mode in the latter case. The combined growth rates and condensation sinks required a condensable vapor concentration of $10^8\text{--}10^9 \text{ mol cm}^{-3}$, while a vapor source rate was estimated to be $2\text{--}3 \times 10^6 \text{ mol cm}^{-3} \text{ s}^{-1}$. The estimated source rate of 1-nm particles (or in other words, the actual nucleation rate) was between 30,000 and $10^6 \text{ particles cm}^{-3}$ depending on the nucleation event intensity [*Dal Maso et al.*, 2002].

[42] The most comprehensive analysis of the nucleation and vapor source rates required detailed model case studies. The formation and evolution of new coastal particles were examined using the aerosol dynamic and gas-phase chemistry model AEROFOR2 [*Pirjola et al.*, 2002]. The chemistry included sulphur chemistry and a generic unknown species x , produced photochemically from a primary biogenic species y emitted from the shore. In this model, species x is regarded as an insoluble species which becomes internally mixed with more soluble species such as sulphuric acid. In order to replicate the observations of 3 (N_3) and 10 (N_{10}) nm particles after 25 s of plume evolution, a range of nucleation ranges and condensable vapor concentrations was determined. As seen in Figure 8, the possible vapor

concentration covers only a narrow strip from 6×10^9 to $1.1 \times 10^{10} \text{ cm}^{-3}$, and the nucleation rate has to be between 3×10^5 and $4 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$. Especially when N_3 has a value of about $1 \times 10^6 \text{ cm}^{-3}$ (corresponding to the more intense events), the vapor concentration must be $6.6 \times 10^9 \text{ cm}^{-3}$ and the nucleation rate $3 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$, while for a lower value of $N_3 = 2 \times 10^5 \text{ cm}^{-3}$, the vapor concentration must be $1.1 \times 10^{10} \text{ cm}^{-3}$ and the nucleation rate must be $3 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$. In both cases, the model predicts a value of $5 \times 10^7 \text{ cm}^{-3} \text{ s}^{-1}$ for the source rate of the vapor.

[43] The recently developed ternary nucleation theory of *Korhonen et al.* [1999] was further developed for the range of conditions encountered during PARFORCE in order to estimate the nucleation rates from the measured temperature and sulphuric acid, ammonia, and water vapor concentrations [*Kulmala et al.*, 2002]. These results indicate that the observed sulphuric acid concentration of $10^6\text{--}10^7 \text{ molecules cm}^{-3}$, combined with the ammonia concentrations (>10 ppt up to 2 ppb) was always sufficient to account for nucleation the estimated concentration of 1-nm particles. It should be noted that while the given concentrations of sulphuric acid may explain the predicted and required nucleation rates, there is insufficient sulphuric acid vapor to grow these particles to detectable sizes of 3 nm.

5. Mechanisms for Coastal Nucleation

[44] Peak particle number concentrations reach $>10^6 \text{ cm}^{-3}$ during coastal nucleation events, and these can last up to several hours. The measurement point is typically 100 m from the source region during most events. This implies extraordinary source rates of both precursor gases and particles. Modeling of the most likely nucleation mechanism, namely ternary nucleation of sulphuric acid, water, and ammonia suggest that this mechanism is very likely to produce new stable sulphate clusters [*Kulmala et al.*, 2000, 2002], but the measured concentrations are insufficient to grow these particles to detectable sizes of 3 nm. Measurements of the hygroscopic growth factors of new particles corroborate the statement that sulphate precursors do not provide the primary, or necessary, condensable vapor material. The growth factors clearly indicate a very low solubility aerosol in the nanometer size range. Organic material could be ruled out for two reasons: (1) No biogenic VOCs were detected from biogenic emission studies, and (2) VOC reactions are not sufficiently fast to produce the quantity of precursor material required. The model studies suggest a nucleation rate of the order of $10^6 \text{ cm}^{-3} \text{ s}^{-1}$, a vapor concentration of $10^9\text{--}10^{10} \text{ cm}^{-3}$, and a vapor source rate of $5 \times 10^7 \text{ cm}^{-3} \text{ s}^{-1}$.

[45] Given that iodine species were observed by be enhanced during low tide, laboratory experiments were conducted to investigate if the photolysis of CH_2I_2 , in the presence of ozone, could produce a significant particle yield [*Hoffmann et al.*, 2001]. These experiments also measured the chemical composition of produced particles using mass spectrometric techniques. During the experiments, it was found that massive amounts of particles were produced very rapidly. The on-line mass spectrometric investigations suggest that the aerosol formed from the CH_2I_2 photolysis is composed of iodine oxides. On the basis of these results and available literature data [e.g. *Cox et al.*, 1999] *Hoffmann*

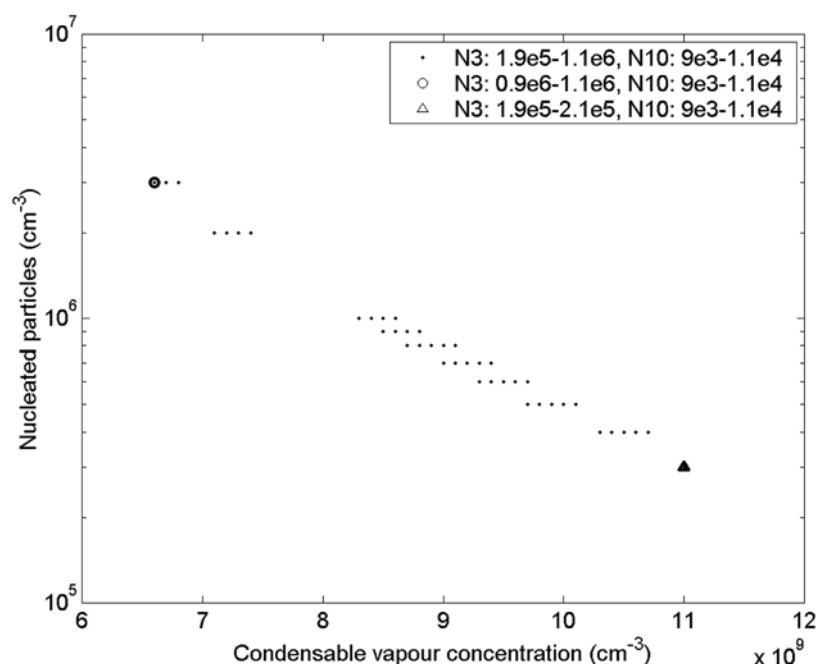


Figure 8. Possible combinations of the nucleated particle concentration and the condensable vapor so that after 25 s (~ 0.4 min) simulation the concentration of particles with diameter >3 nm (N_3) is in the range of $200,000$ – $1,000,000$ cm^{-3} and of particles with diameter >20 nm (N_{10}) is in the range of $9,000$ – $11,000$ cm^{-3} . For the circle, $N_3 \approx 1,000,000$ cm^{-3} , for the triangle, $N_3 \approx 200,000$ cm^{-3} .

et al. [2001] suggested that the photolysis of CH_2I_2 in the presence of O_3 leads to the production of I_2O_4 in the aerosol phase, resulting from the self-nucleation of OIO.

[46] The photodissociation of alkyl iodides to produce I atoms followed by the rapid reaction of I with ozone to form IO radicals, have been described previously [Vogt *et al.*, 1999; Sander *et al.*, 1997; McFiggans *et al.*, 2000; Davis *et al.*, 1996] while the production of OIO from the self reaction of IO has been discussed by Cox *et al.* [1999]. One must also recall that there have been some events that have indicated an unaccounted for loss of OH during nucleation events [O'Dowd *et al.*, 1999a; Berresheim *et al.*, 2002] and that this may very likely result from the rapid titration of OH/ HO_2 by iodine leading to HI and HOI which are also likely to condense into the aerosol phase. It should be borne in mind, however, that these initial laboratory experiments [Hoffmann *et al.*, 2001] were not conducted under atmospheric conditions. Thus, it cannot be conclusively stated at this stage that iodine is involved in the actual nucleation mechanism.

[47] From the combined field studies, laboratory studies, and theoretical simulations, we are left with two best-guess possible formation mechanisms for coastal particle production: (1) Stable sulphate clusters are formed via ternary nucleation of sulphuric acid, ammonia, and water vapor, and subsequently, the rapid condensation of OIO/ I_2O_4 (and/or HI and HOI) is required to produce detectable particles; or (2) the self reaction of iodine dioxide is responsible for both the nucleation and growth mechanisms. In both cases, low hygroscopic growth factors will result if the production does not coincide with the diurnal peak in sulphuric acid production. If the nucleation event coincides with this peak production period, then the

sulphuric acid only contributes to, and does not dominate, the growth.

6. Spatial Extent Of Particle Production and Growth Into Radiatively Active Sizes

[48] One of the objectives of this study was to study the spatial extent of the nucleation events along the west coast of Ireland in order to rule out this phenomenon as being Mace Head specific. One spatial mapping flight along the coastline was conducted, albeit during one of the least productive events. Because of timing of aircraft availability, the flights were conducted during a period of minimal tidal amplitude, and consequently, exposure of biota. During the mapping flight, a very modest event, with $10,000$ particles cm^{-3} , was observed at Mace Head and particle production was observed along more than 300 km of coastline. Many production regions produced particle concentrations 10–15 times higher than at the Mace Head station, indicating that there were significantly stronger sources other than the Mace Head Station [O'Dowd, 2002].

[49] The second objective of deploying an aircraft was to examine the growth of new particles in the coastal plume as it advected away from the source region. A second flight was conducted to initially map the production region north of Mace Head and locate the coastal plume to be tracked, in a pseudo-Lagrangian manner, off the coast and out over the north Atlantic northwest of Ireland. Such a scenario involved a southerly airflow parallel to the coastline. As in the mapping flight, large source regions were encountered far away from Mace Head, with concentrations reaching 10^5 – 10^6 cm^{-3} near the source. The coastal plume encountered extended more than 60 km in width and was

sampled as it evolved more than 250 km offshore. The vertical extent of the plume was observed to reach the boundary layer height of 1000 m, despite slightly stable meteorological conditions. During this plume evolution, the growth of the new particle mode from sizes <5 up to >40 nm was observed. After the plume had evolved for 3–3.5 hours, increases in scattering coefficients, by a factor of approximately 2, were observed along with significant increases in cloud condensation nuclei. These results confirm that the spatial extent of tidal related particle production is regionally significant, and after a few hours, the growth of these recently formed coastal aerosols significantly increase the concentration of radiatively active aerosol particles.

[50] The AERFOR2 Lagrangian model [Pirjola *et al.*, 2002] was used to simulate the growth and evolution of new particles into radiatively active sizes for a period longer than what was possible to measure using an aircraft. The scenario used was similar to that observed on the aircraft Lagrangian flight; however, clean marine background conditions were used as well as polluted conditions [Pirjola *et al.*, 2002], and the air was allowed to advect over the source region and back out over the ocean for 4 days. For the base case study, the nucleation rate was $3 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$, $x = 1.1 \times 10^{10} \text{ cm}^{-3}$, $y = 2.3 \times 10^{10} \text{ cm}^{-3}$, and $k = 5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A significant fraction of the new particles were predicted to survive to grow into cloud condensation nuclei (CCN) sizes for supersaturations typically encountered in boundary layer clouds during 3 days of clear-sky conditions, thus contributing to the indirect radiative effect of aerosols. In all simulated cases, an increase of more than 100% in CCN concentration, for supersaturations >0.35% was observed, despite the insoluble nature of the new particles. During advection out over the ocean, these new condensation sites gain more soluble mass from DMS oxidation productions, thus increasing the CCN potential of the coastal nuclei.

7. Conclusions

[51] Biogenic coastal aerosol formation events occur approximately 90% of days of the year around the western coastline of Europe. These events occur during daylight hours often coinciding with low tide. The source of aerosol precursors is the exposed tidal zone, at least at Mace Head. Nucleation occurs simultaneously all along the coastline suggesting that coastal regions provide a very significant source of natural aerosol particles. During these events, peak aerosol concentrations can exceed 10^6 cm^{-3} during nucleation bursts which can last from 2–8 hours. Measured formation rates of detectable particle sizes (i.e. $d > 3 \text{ nm}$) are of the order of 10^4 – $10^5 \text{ cm}^{-3} \text{ s}^{-1}$, while nucleation rates of new particles are of the order of 10^5 – $10^6 \text{ cm}^{-3} \text{ s}^{-1}$.

[52] Nucleation is observed for sulphuric acid concentrations $>2 \times 10^6 \text{ molecules cm}^{-3}$; however, no correlation existed between peak sulphuric acid concentrations and low tide occurrence or nucleation events. Growth factor analysis of recently formed 8-nm particles indicates that these particles must comprise some species significantly less soluble than sulphate aerosol. The growth-factor data, combined with the lack of detectable VOC emissions from coastal biota, the strong emission of halocarbons, the tidal

related cycle in halocarbons and IO, and the fingerprinting of iodine in recently formed particles, suggest that the most likely species resulting in the growth of new particles to detectable sizes is a condensable iodine vapor. This is corroborated by laboratory experiments. It remains an open question whether nucleation is driven by self nucleation of iodine vapors, or whether first, stable clusters are formed through ternary nucleation of sulphuric acid, ammonia and water vapor, followed by condensation growth into detectable sizes by condensation of iodine vapors.

[53] Sulphuric acid concentrations reached levels in excess of $10^7 \text{ molecules cm}^{-3}$ on 73% of the measurement days. Acid concentrations on polluted days exceeded $10^8 \text{ molecules cm}^{-3}$. OH concentrations had peak values of 2 – $4 \times 10^6 \text{ molecules cm}^{-3}$. MSA concentrations exhibited peak values in marine air masses with concentrations between 2 – $4 \times 10^6 \text{ molecules cm}^{-3}$. A significant source of nighttime sulphuric acid was observed, suggesting the presence of another important SO_2 oxidant.

[54] Preliminary modeling studies have been conducted to examine the yield of radiatively active (accumulation mode sized) particles. Initial predictions for cloud free conditions suggest that after 3–4 days of advection out over the ocean following nucleation in the coastal zone, the background cloud condensation nuclei concentration can increase by 100%, consequently, coastal biogenic aerosol may contribute significantly to the natural background aerosol population and the radiative forcing of aerosols.

[55] While considerable advances have been achieved under PARFORCE, there are still many unanswered questions. Fundamentally, the actual nucleation mechanism has not been elucidated; however, there are two very likely mechanisms that require testing in more detailed experiments with fast response and more sensitive instrumentation to measure gas-phase iodine and new particle chemical composition. Apart from understanding the actual nucleation and growth mechanisms, a future study should be dedicated to understanding the regional impact of these coastal particles and their contribution to the natural background aerosol distribution, their impact on radiative properties, and the relationship between the flux of biogenic halogen species and the flux of new particles into the atmospheric boundary layer.

[56] **Acknowledgments.** This work was supported by the European Union under contract ENV4-CT97-0526 (PARFORCE). Flight hours were funded under the EU STAAARTE programme. TNO Physics and Electronic Laboratory received additional support from the Netherlands Ministry of Defence. The efforts of all the contributors to PARFORCE are acknowledged.

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