

Meteorological influences on coastal new particle formation

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[1] The meteorological situation at the midlatitude coastal station of Mace Head, Ireland, is described based on observations during the New Particle Formation and Fate in the Coastal Environment (PARFORCE) experiments in September 1998 and June 1999. Micrometeorological sensors were mounted near the shore line on a small mast with a height of 3 m and on a 22 m high tower at about 100 m away from the sea. Turbulent fields of wind speed, air temperature, and water vapor were measured. Parameters such as the friction velocity, drag coefficient, kinematic fluxes of heat and water vapor, and various variances were derived. The influence of meteorological parameters on coastal nucleation events is examined, and it is found that the occurrence of nucleation is, more or less, independent of air mass origin and is primarily driven by the occurrence of exposed shore areas during low tide and solar radiation. Micrometeorological influences were also examined in terms of promoting particle production events in this environment. A positive correlation was found between kinematic heat flux and particle production probability. In contrast, a strong negative correlation was found between production probability and both kinematic water vapor fluxes and relative humidity. These results indicate that the occurrence of new particle production events in the coastal zone are most probable during conditions when the shore area containing coastal biota has dried out and the biota are exposed directly to the solar radiation flux and increased shore, or surface, temperatures. These conditions correspond to drying and stressing of the biota, which is known to increase the emissions of biogenic vapors. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 3307 Meteorology and Atmospheric Dynamics: Boundary layer processes; 3322 Meteorology and Atmospheric Dynamics: Land/atmosphere interactions; **KEYWORDS:** aerosol, nucleation, micrometeorological fluxes, coastal

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1. Introduction

[2] Nucleation events have been repeatedly observed at coastal sites during low tide [e.g., O'Dowd *et al.*, 1999, 2002a], but the underlying processes and the conditions leading to such events are not completely understood. Nucleation theories are generally applied to "average" conditions in the marine boundary layer (MBL). Pirjola *et al.* [2000] show that in the marine boundary layer at midlatitudes nucleation of sulphuric acid and water is very unlikely to occur, except for extremely high concentrations of gases or low concentrations of sea spray aerosol. Binary nucleation does occur for polar marine conditions due to

lower temperatures, and is enhanced due to turbulent fluctuations. Pirjola *et al.* [2000] do, however, illustrate that ternary nucleation of sulphuric acid, water and ammonia is possible but these particles are unlikely to grow to detectable sizes of greater than 3 nm (corresponding to new particle production as opposed to nucleation of stable embryos) under typical concentrations of dimethyl-sulphide. Kerminen and Wexler [1994] have highlighted the importance of rapidly changing natural environmental conditions (such as cooling of rising air parcels) which leads to timescales promoting nucleation events. Easter and Peters [1994] suggested that small scale fluctuations of temperature about mean values and associated fluctuations of relative humidity, normally associated with atmospheric turbulence, may cause second-order effects to

dominate over mean behavior. Model calculations by Pirjola *et al.* [2000] lead to the conclusion that both of these effects could promote particle formation in the MBL.

[3] The frequent occurrence of nucleation, or specifically, new particle production events, at coastal sites during low tide [O'Dowd *et al.*, 2002a] suggests the release of biogenic gaseous species from the tidal flats and the coastal biota at high enough concentrations to produce regular and significant nucleation and particle production events. These regular events provide an opportunity to study processes promoting nucleation in the coastal atmosphere. To better understand the nucleation processes, two comprehensive field experiments were undertaken at the Mace Head Research Station (Ireland) as part of the PARFORCE project on New Particle Formation and Fate in the Coastal Environment [O'Dowd *et al.*, 2002a]. At Mace Head, the wind direction is the main indicator for the occurrence of enhanced concentrations of condensation nuclei (CN) [O'Brien *et al.*, 2000]. It should be noted that the analysis conducted by O'Brien *et al.* [2000] focused on the concentrations of particles larger than 10 nm and consequently, the results are biased toward these larger nucleation mode particles rather than the smaller, and younger, particles in the 3–10 nm size range which are the focus of this study.

[4] Based on wind directions and air mass trajectories, O'Dowd *et al.* [2002b] classified particle production events observed during PARFORCE in four types. In brief, particle production of type I occurred in clean marine air, with wind directions from the south to northwest sector and air masses transported over a single tidal region at a 100 meters or less from the measurement station. Type II events were also associated with clean marine air, but with wind directions in the northwest to north sector, passing over more than one tidal region and with a fetch over land of typically 10–20 km. Type III events occur in polluted air from east to southerly directions, advected over a tidal region at 2–3 km from the station. Type IV events correspond to situations where the air has not advected over tidal regions and were regarded as null events. The particle concentrations and size distributions for each event type are typically different and are discussed in detail in O'Dowd *et al.* [2002b]. In this study, the relationship between meteorology and particle production events are studied in more detail and, in particular, the role of micrometeorological fluxes is examined.

[5] Apart from the synoptic meteorological situation, the most important factor affecting micrometeorological fluxes at Mace Head is the land or ocean surface, which properties, expressed in the roughness length, are different for each wind direction and, for onshore winds, also change with tidal amplitude. The current analysis is focused on the events occurring in clean marine air (e.g., type I and type II particle production events) and onshore winds with the shortest distance to the tidal flats. Obviously, the micrometeorological results presented here apply only to the specific site and would vary with the measurement location. However, the issues are common for many coastal sites used for atmospheric research, where the coastline constitutes a sharp separation between

extensive water and landmasses with significantly different physical properties.

2. Micrometeorological Parameters

[6] The micrometeorological parameters that are of interest for studies of nucleation and particle production are the variances of temperature and relative humidity, i.e., indications of the fluctuations about the mean that may influence nucleation rates [Easter and Peters, 1994]. The friction velocity and drag coefficient are indicators of vertical mixing and near-surface turbulent transport, as are momentum, heat and water vapor fluxes. Discussions of the micrometeorological parameters can be found in text books [e.g., Businger, 1973; Panofski and Dutton, 1984; Arya, 1988; Stull, 1988].

[7] The wind speed is expressed in its three mean orthogonal components \bar{U} , \bar{V} and \bar{W} , where \bar{U} is the mean stream-wise horizontal component, \bar{V} is the mean lateral velocity component, and \bar{W} is the mean vertical velocity component. An orthogonal coordinate system is chosen such that the x axis is along the stream wise wind speed component \bar{U} , and \bar{V} and \bar{W} are zero. Other parameters used in this work are the air temperature t and the specific humidity q . Each quantity x is composed of its mean, \bar{x} , and turbulent, x' , components: $x = \bar{x} + x'$. The mean values of x' are zero. The variance is given by:

$$\sigma_x^2 = \langle x'x' \rangle \quad (1)$$

where $\langle \rangle$ indicates a time average. Time and space averages are assumed identical (Taylor's hypothesis).

[8] Derived parameters are the friction velocity, the drag coefficient, surface roughness and momentum, heat and water vapor fluxes.

[9] The friction velocity, u_* , is defined as:

$$u_*^2 = -\langle u'w' \rangle \quad (2)$$

where $\langle u'w' \rangle$ is the average value of the covariance between the horizontal and the vertical velocity components. The friction velocity is a velocity scaling parameter that is used, e.g., to describe the variation of the wind speed with the height z above the surface:

$$\bar{U} = \frac{u_*}{\kappa} \ln \left(\frac{z}{z_0} \right), \quad (3)$$

where κ is the Von Karman constant ($\kappa = 0.4$) and z_0 is the aerodynamic roughness length, defined as the height where the wind speed becomes zero. The value of z_0 depends on the vertical extent of roughness elements, their horizontal surface area, and can vary from 10^{-5} m to 100 m [Stull, 1988]. For the Mace Head site roughness lengths can be expected to vary between 10^{-4} m (calm sea) and about 10^{-1} m (over land with rocks) [Kunz *et al.*, 2000]. Expressions for z_0 are given by Stull [1988]. In this study, the roughness length was calculated using:

$$z_0 = ze^{-\kappa/\sqrt{C_D}} \quad (4)$$

The drag coefficient, C_D , is the friction velocity normalized to the macroscopic wind speed \overline{M} [cf. *Stull*, 1988]:

$$C_D = \frac{u_*^2}{\overline{M}^2} \quad (5)$$

In the literature, values for C_D are usually given at a standard height of 10 m, in thermally neutral conditions. Other parameters of interest for this study are the kinematic heat flux $\langle w' t' \rangle$ and kinematic water vapor flux $\langle w' q' \rangle$, further referred to as heat flux and water vapor flux.

[10] Equation (3) describes a simple logarithmic profile that applies in neutral conditions. For nonneutral conditions correction terms should be applied [*Stull*, 1988]:

$$U = \frac{u_*}{\kappa} \left[\ln\left(\frac{z}{z_0}\right) - \Psi_m\left(\frac{z}{L}\right) \right], \quad (6)$$

where $\Psi_m\left(\frac{z}{L}\right)$ is the stability correction term, L is the Monin-Obhukov length. The value of L depends on the thermal stratification, positive values indicate stable stratification, negative values indicate unstable stratification. Stable stratification prohibits vertical mixing, whereas during unstable stratification the air is well mixed throughout the boundary layer. The conditions at Mace Head were often neutral or close to neutral.

3. Instrumentation and Measurements

[11] The PARFORCE field experiments were undertaken at the Mace Head Research Station located on the western coast of Ireland (53°20'N, 9°54'W) in September 1998 and in June 1999. A detailed description of the station and measurements at Mace Head is given by *Jennings et al.* [1991, 1998]. 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. The coast is covered with rocks and boulders to the west and north west and with large tidal flats to the southeast. Hence the coastline constitutes a transition from a smooth water surface modulated by moving waves, the rough surf zone and finally a very rough stationary land surface. The changes in surface roughness and the sloping land surface obviously generate strong variations in the micrometeorological properties, causing a nonstationary situation in which commonly used profile formulations do not apply. Therefore, two suites of micrometeorological sensors were installed, one very close to the tidal region at 3 m and the other on a 22 m tower 100 m from the tidal region, to characterize the meteorological properties during the PARFORCE experiments. Local tidal amplitudes were calculated using the TIDECALC tidal prediction system of the U.K. Hydrographic Office. During the second experimental period a simple tide sensor, measuring water column pressure, was installed [cf. *Kunz et al.*, 2000].

3.1. Meteorological Instrumentation

[12] Standard meteorological parameters available at Mace Head are wind speed, wind direction, relative humidity, air temperature, and solar radiation (total and ultra-

violet), which are measured at the uphill laboratory at 300 m from the coastline. For PARFORCE, these were expanded with micrometeorological measurements comprising fast response measurements of the three-dimensional (3-D) wind field and the air temperature using an asymmetric Gill 3-D ultrasonic anemometer (further referred to as sonic), and water vapor fluxes determined with an Advanet CO₂/H₂O fluctuation sensor, an IR absorption device.

[13] One of the sonics was mounted close (a few meters) to the high water line, on a small mast at a height of 3 m above the surface. At low tide the distance to the water increased to approximately 100 m. Also, the Advanet was mounted on this mast, which was further equipped with a Rotronic sensor for mean air temperature and relative humidity.

[14] The other sonic was mounted on the Mace Head research tower, about 100 m from the water, on an extension with a length of 1.85 m to reduce the effect of flow distortion caused by the tower structure. During the 1998 PARFORCE experiments this sonic was mounted at a height of 18 m above the surface. Because the analysis showed that at certain wind directions the data were influenced by flow distortion induced by the tower structure, for the June 1999 experiments the instrument was mounted on the top of the tower, at a height of 22 m.

3.2. Data Recording and Processing

[15] The signals from the sonics and from the Advanet were recorded with a repetition rate of 20 Hz, 24 hours per day. The data from the other instruments were recorded with a repetition rate of 1/3 Hz. Before further processing, an alignment procedure was applied to the ultrasonic anemometer data to factor out the mean lateral and vertical wind components. The alignment procedure provides the streamwise wind component and the azimuth and elevation angles of the wind vector. Subsequently, the covariance matrices of u' , v' , w' , t' , and q' at 3 m and of u' , v' , w' and t' at 18/22 m were calculated as 30-minutes averages. Elements of these matrices were used to calculate the friction velocity, stability, drag coefficient, surface roughness and fluxes of heat and water vapor in addition to the mean value and the standard deviation of each measured component.

4. Results

[16] In this study, a brief summary of air mass trajectories and synoptic weather conditions is given and the influences of micrometeorological parameters on new particle formation is presented. As mentioned previously, micrometeorological measurements were taken at 3 m and 22 m, with the 3 m mast being located close to the high water mark, and differences in meteorological parameters are expected between these two levels. Since the focus of this study is on the micrometeorological influences on new particle formation and the source region of coastal new particles is considered to be the tidal area during the occurrence of low tide, measurements of micrometeorological parameters are presented primarily for the location nearest to the tidal region. A full meteorological characterization of the Mace Head station and differences observed between the 3 and 22 m levels are presented by *Kunz and de Leeuw* [2000]. Two PARFORCE field campaigns were conducted, one

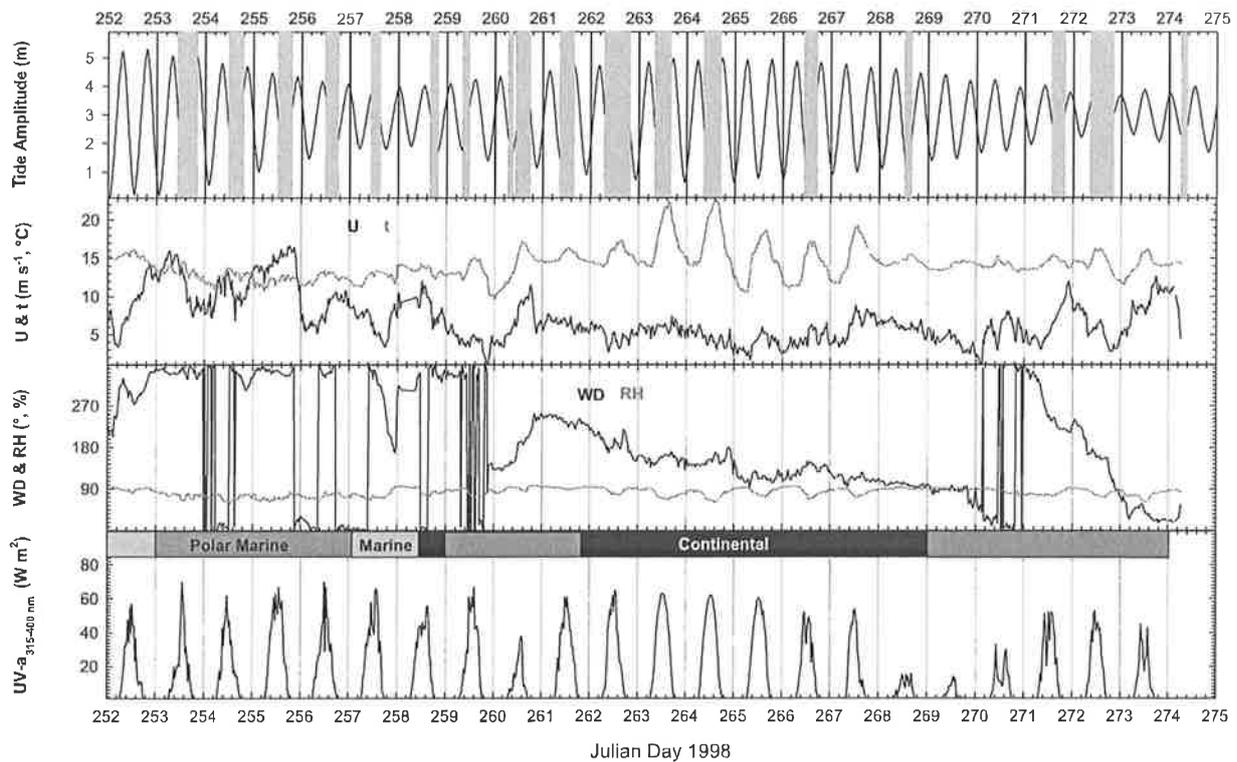


Figure 2. Tidal amplitude, particle production events (gray bars on top plot), wind direction, wind speed, air temperature, relative humidity and solar radiation for the September 1998 PARFORCE field campaign. Also highlighted are the periods for polar marine, marine and continental air masses.

were also common during the polluted periods. These air masses can be classified as modified maritime in a strict sense; however, for the purpose of this study, all polluted air masses are labeled continental. Boundary layer structure during the continental air mass conditions are often more complex than those occurring in marine air masses and sometimes multiple (4–5) layers can be observed within the boundary layer itself [Kunz *et al.*, 2002]. Particle production was observed in all air masses, including even the most polluted. As discussed by O’Dowd *et al.* [2002b], regardless of air mass origin, when the air advected over tidal regions during conditions of solar radiation, new particle production was observed. Continental air masses had the least amount of cloud associated with them, with the only cloud-free days also occurring during continental air mass conditions.

4.2. Meteorological Parameters

[18] Meteorological conditions, tidal amplitude and occurrence of new particle formation events during the 1998 campaign are presented in Figure 2 along with air mass trajectory characterization. As seen in the figure, tidal amplitude not only has a daily cycle, but also has a 2 week cycle in the degree of tidal amplitude variation. The beginning of the campaign was characterized by a difference of >5 m (as calculated by the TIDECALC program) between low and high water marks. It should be noted that, given the terrain at Mace Head, this corresponds to a shore coverage (or lack of coverage) between low and high tide of the order of 100 m. This period is also characterized by high wind speeds (>16 m s⁻¹) and relative humidities of the order of

90–95% but decreasing to 75–85% in the afternoon. Air temperature was of the order of 12–15°C and cloud cover was moderate (from examination of the UV radiation data). Despite moderate cloudiness and the high winds concomitant with high aerosol condensation sink resulting from the enhanced sea-spray generation, particle production was quite strong on these days (JD 253–256) with production events lasting up to 7 hours per day. As the tidal amplitude reduces over the following days (up to JD 259), the duration of the production events seems to reduce, and increase later as tidal amplitude increases around JD 261–264. The period around JD 262–264 corresponds to continental air under cloud free conditions, lower wind speeds, and elevated peak daytime temperatures of 23°C. No particle production was observed on days JD 269–270. These days corresponded to winds from the north to east of the station and very low levels of solar radiation. Regions from the northeast of the station are regions without any, or with reduced, tidal zones.

[19] A similar frequency of occurrence of particle production events is also seen for the 1999 campaign (Figure 3) and they occur under similar conditions. There is less coherence between tidal amplitude and event duration during the 1999 campaign. In general, and despite being the middle of the summer period, lower temperatures of the order of 10–15°C were encountered compared to the autumn period, although the peak solar radiation intensity was slightly higher in summer than in autumn. No significant difference was seen in wind speed between both campaigns, although strongest winds did occur during the

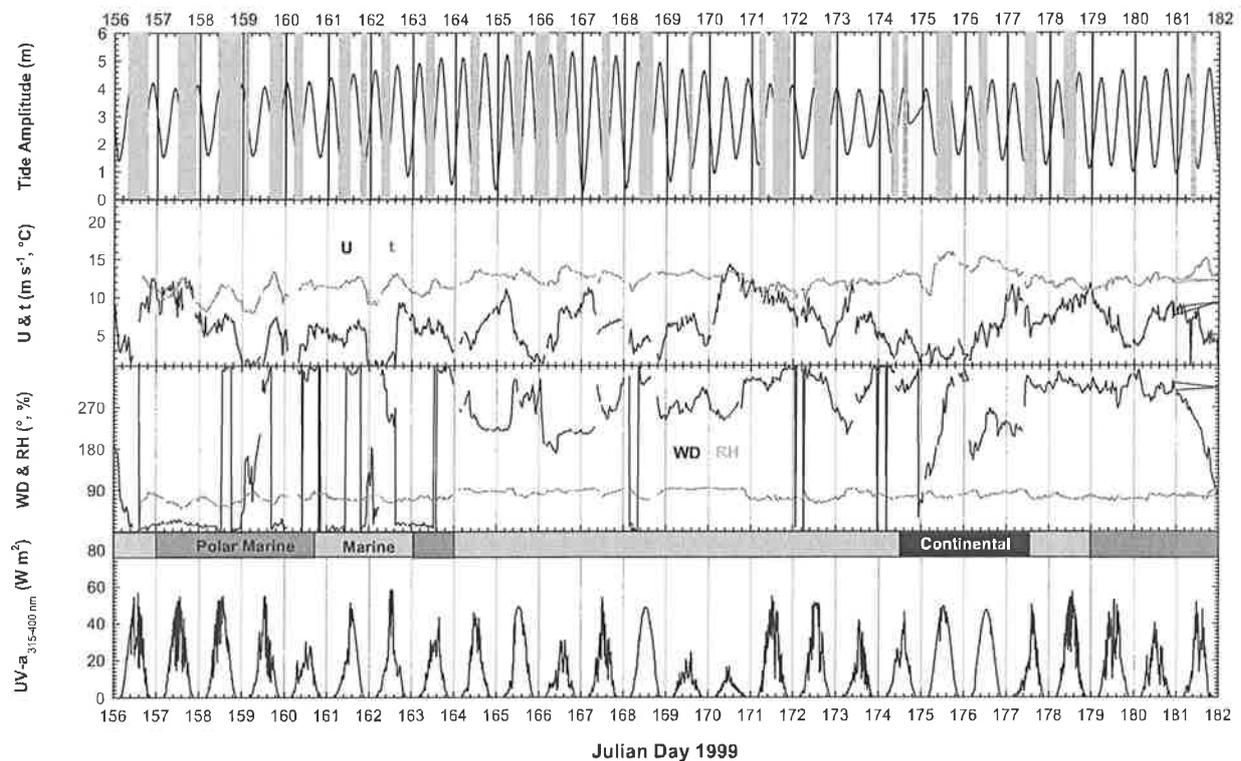


Figure 3. Tidal amplitude, particle production events (gray bars on top plot), wind direction, wind speed, air temperature, relative humidity and solar radiation for the June 1999 PARFORCE field campaign. Also highlighted are the periods for polar marine, marine and continental air masses.

autumn period. During the 1998 campaign, mean wind speeds were 7.3 m s^{-1} with maximum of 16.6 m s^{-1} , while during the 1999 campaign, mean wind speed was 6.2 m s^{-1} with a maximum of 14.3 m s^{-1} . Relative humidity was also lower during the 1999 campaign with a mean value of 76.6% and a range of humidities from 31% to 94% compared to a mean of 83% in the 1998 campaign, ranging from 60% to 97%. Temperature during the 1999 campaign was lower with a mean value of 11.8°C and a minimum and maximum of 7.9°C and 16°C , respectively, compared to 14.3°C , 9.8°C and 22.6°C during the 1998 campaign.

4.3. Micrometeorological Parameters

[20] In Figures 4 and 5, wind speed, friction velocity u_* , water vapor flux $\langle w'q' \rangle$, heat flux $\langle w't' \rangle$ and drag coefficient (C_D) are presented along with tidal amplitude and event occurrence. u_* , as expected, reflects changes in wind speed as well as variations associated with changes in wind direction (and consequently, surface roughness). The highest values occur for the highest wind speed confirming that the primary influence on u_* is wind speed. Similarly, for a given wind direction, C_D is primarily influenced by wind speed, with the highest drag coefficients occurring during periods of highest wind speed. Wind direction has a significant influence on C_D with large increases in C_D seen during the continental air mass conditions (i.e., airflow over land with relatively high surface roughness) when compared to marine air masses (i.e., westerly airflow over the ocean), despite the higher wind speed generally observed for the marine air (e.g., JD 170–177, 1999).

[21] While wind speed and wind direction influence most the drag coefficient, under quasi-stationary airflow in marine air, the tidal amplitude also has an influence on C_D . This is particularly evident for the marine air masses and persistent northwesterly airflow observed from JD 178 to JD 182 (see Figure 6). Clearly, there is a noticeable enhancement in the drag coefficient corresponding to low tide, indicating the enhanced surface roughness in the tidal zone since more of the rocky shoreline is exposed as the water recedes. These data indicate the measurement footprint is over the water during high tide and over the exposed shoreline during low tide.

[22] Heat and water vapor fluxes showed significant variability throughout both periods (Figures 4 and 5): during the 1998 campaign, mean water vapor fluxes were $0.038 \text{ g kg}^{-1} \text{ m s}^{-1}$ with a minimum of $-0.14 \text{ g kg}^{-1} \text{ m s}^{-1}$ and a maximum of $0.51 \text{ g kg}^{-1} \text{ m s}^{-1}$ (standard deviation $\sigma = 0.05$). Heat fluxes ranged from $-0.27^\circ\text{C m s}^{-1}$ to $+0.26^\circ\text{C m s}^{-1}$ with a mean of $0.007^\circ\text{C m s}^{-1}$ ($\sigma = 0.0712$). During the 1999 campaign, mean water vapor fluxes were of the order of $0.025 \text{ g kg}^{-1} \text{ m s}^{-1}$, with a minimum of $-0.178 \text{ g kg}^{-1} \text{ m s}^{-1}$ and a maximum of $+0.23 \text{ g kg}^{-1} \text{ m s}^{-1}$ ($\sigma = 0.038$). Heat flux was $0.024^\circ\text{C m s}^{-1}$ with a minimum of $-0.31^\circ\text{C m s}^{-1}$ and a maximum of $+0.34^\circ\text{C m s}^{-1}$ ($\sigma = 1.146$, indicating the large degree of variability in heat flux). Maximum water vapor flux values were generally encountered for periods with high wind speeds, although it is difficult to determine other meteorological parameters that influence the water vapor flux from the data presented. The water vapor flux was generally near zero at

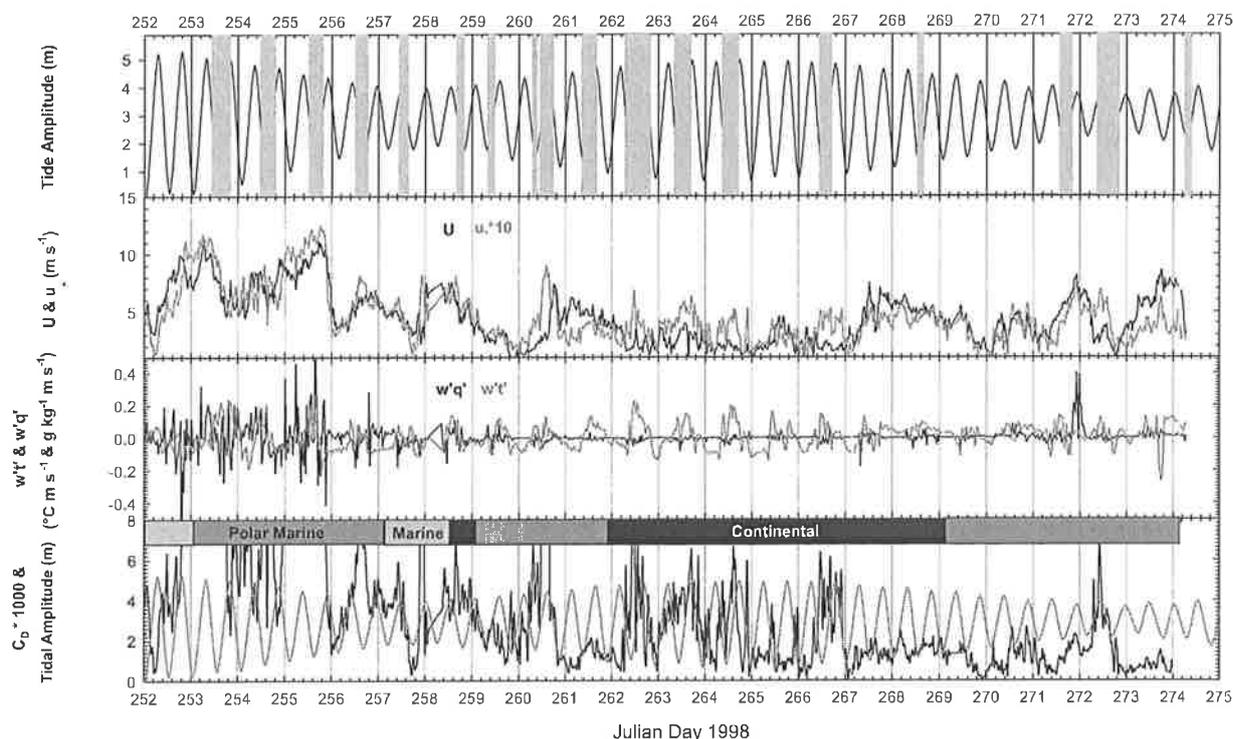


Figure 4. Tidal amplitude, particle production events (gray bars on top plot), wind speed, friction velocity u_* , kinematic water vapor flux $\langle w'q' \rangle$, kinematic heat flux $\langle w't' \rangle$ and drag coefficient for the September 1998 PARFORCE field campaign. Also highlighted are the periods for polar marine, marine and continental air masses.

nighttime suggesting that solar irradiation may have an important influence on the water vapor flux.

[23] Heat flux, on the other hand, generally shows a negative flux during periods of high tide and maximum values during periods of low tide. One clear example of this is presented in Figure 7 for JD 163 in 1999. Also shown are vertical wind velocity variances $\langle w'w' \rangle$ and tidal amplitude. Also shown is the period during which new particle formation occurs. Vertical wind velocity variances are seen to remain constant throughout the day, even during low tide periods, suggesting that the enhanced drag during low tide has little effect on the turbulent vertical wind velocity component. The water vapor flux was positive and steady for the first 8 hours of the day and increases slowly in the late afternoon, decreasing again toward nighttime. Heat flux, on the other hand, is clearly negative during periods of mid-to-high tide conditions and, during the daytime low tide periods, flips over to a clear positive heat flux. The period of positive heat flux corresponds to the period of new particle production, suggesting some link between the two processes.

5. Micrometeorological Variations and Formation of New Particles

[24] As discussed by O'Dowd *et al.* [2001a, 2001b], the formation of new particles is photochemically induced and mainly takes place during low tide; however, the mechanisms leading to particle production are not completely understood. The question thus arises: What initiates a

particle production event? Or, what other requirements are necessary? While solar radiation and shore exposure are the two most clear conditions promoting coastal new particle formation, other micrometeorological processes may also be required to promote particle production. The previous section illustrated the increase in drag coefficients during low tide conditions. This increase in drag coefficient may be associated with an increase in turbulent fluxes and turbulent intensity which are expected to promote nucleation [e.g., Easter and Peters, 1994; Nilsson and Kulmala, 1998; Pirjola *et al.*, 2000]. In order to explore the influence of micrometeorological processes on coastal nucleation and particle production, the potential correlation between particle production event occurrence and meteorological flux parameters is investigated more closely.

[25] Initial examination of the relationship between the concentration, or intensity, of particle production and meteorological parameters proved fruitless, possibly due to the high degree of nonlinearity in the particle production process along with the large amount of variables that can influence emissions (e.g., tidal amplitude, solar intensity, aerosol condensation sinks, different source strengths associated with different wind sectors). Nevertheless, some covariance between micrometeorological parameters and particle production is evident from Figures 4, 5 and 7. In order to get a more quantitative picture of the influence of micrometeorological processes on particle production, the probability of particle production was examined as a function of flux parameter. For this exercise, the probability of particle production was defined as the number of data points

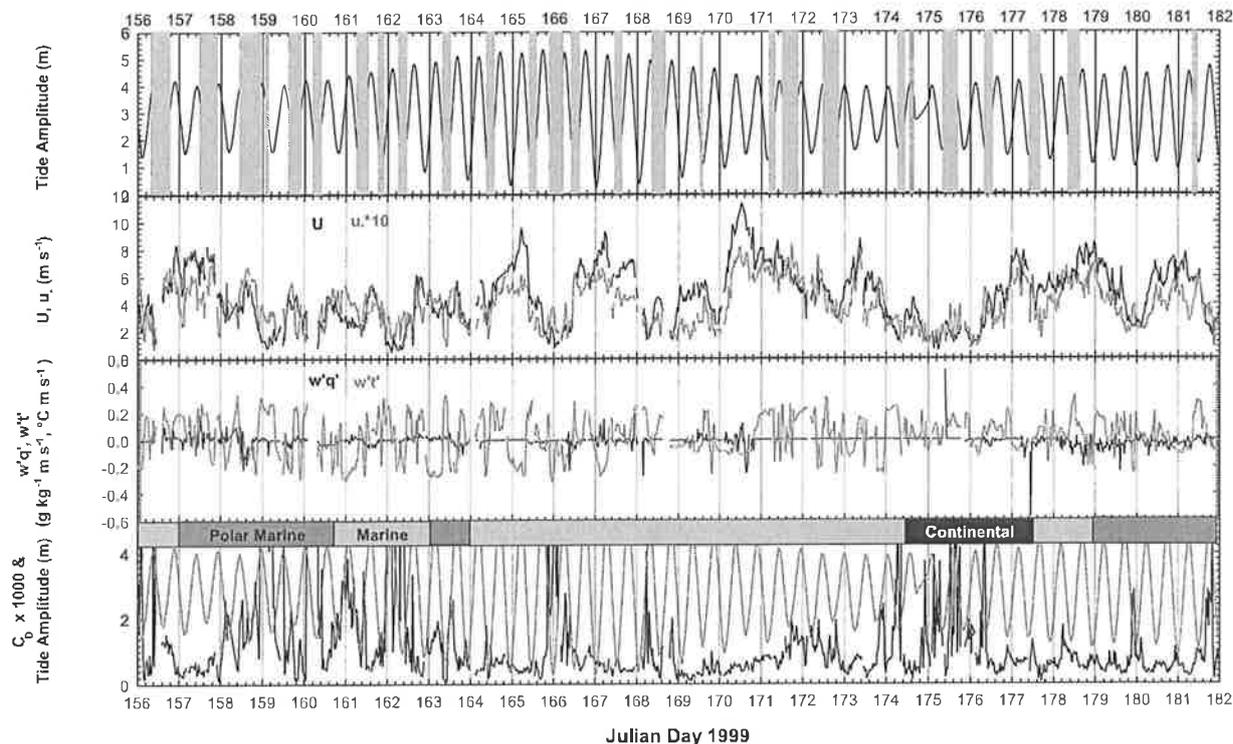


Figure 5. Tidal amplitude, particle production events (gray bars on top plot), wind speed, friction velocity u_* , kinematic water vapor flux $\langle w'q' \rangle$, kinematic heat flux $\langle w't' \rangle$ and drag coefficient for the June 1999 PARFORCE field campaign. Also highlighted are the periods for polar marine, marine and continental air masses.

in a given flux parameter range corresponding to the formation of new particles divided by the total number of data points in that flux parameter range. Each data point corresponds to a 30 minute period required for the flux measurements. New particle production periods were defined as periods containing more than 100 particles cm^{-3} in the 3–20 nm size range [O'Dowd *et al.*, 2002b].

[26] In this analysis, the data set was confined to the west to north wind sector (270° to 360°). The sector control was defined by the 22 m wind direction measurement, while low tide was defined as all periods when the water mark was less than 2 m below the mean sea level water mark. Further, since the particle production events are photochemically driven, only data between 0800 and 1700 were included in

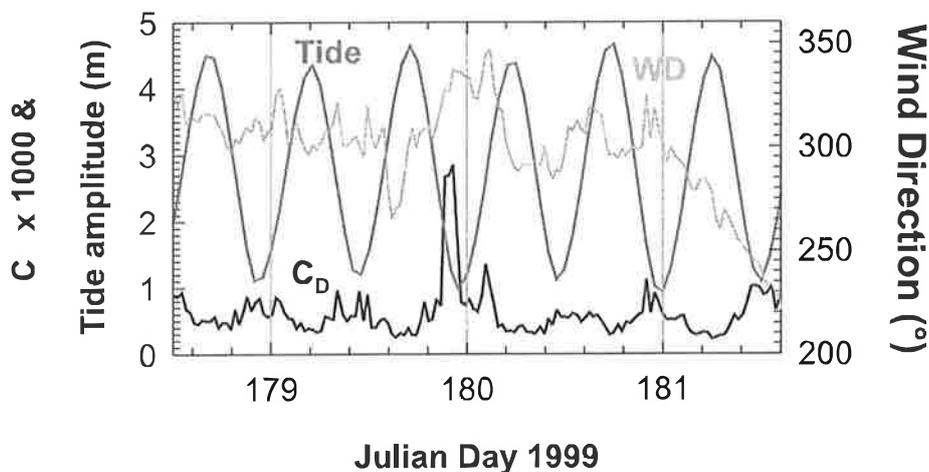


Figure 6. Drag coefficient, wind direction and tidal amplitude for steady marine airflow over the Mace Head station. The high drag coefficient late on JD 179 is due to air moving over a longer land fetch with higher surface roughness.

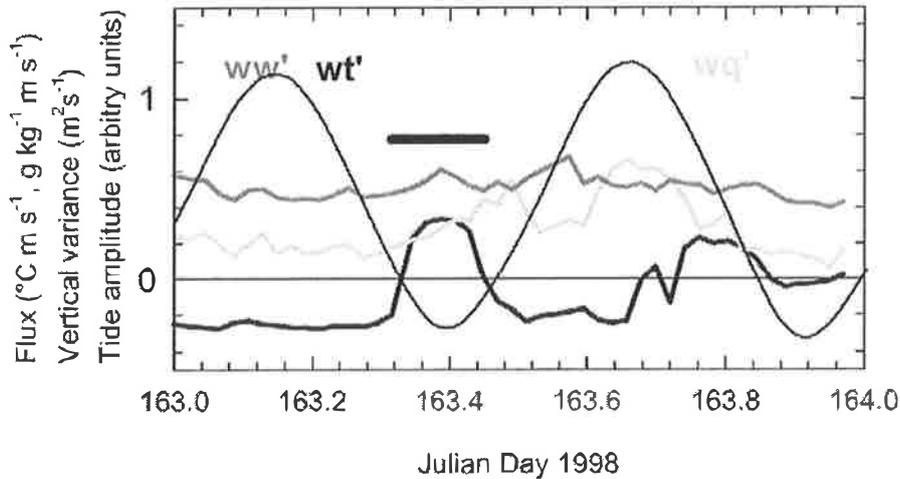


Figure 7. Vertical variances, heat flux, water vapor flux and tidal amplitude during one typical new particle production event at Mace Head. The solid black horizontal bar marks the occurrence and duration of the particle production event on this day.

the analysis. The total number of data points analyzed was greater than 300.

[27] The results of this exercise show that particle production probability is independent of temperature variances with a correlation coefficient of $r^2 = 0.003$ at the 22 m level and 0.004 at the 3 m level. Also, there is little correlation between particle production probability and vertical wind velocity variances with a correlation coefficient of $r^2 = 0.23$ at the 3 m level; although a more significant correlation was observed at the 22 m level with $r^2 = 0.54$, there was no clear relation. The relationship between particle production probability and heat flux for the 3 m (Figure 8) and 22 m (Figure 9) measurement points displayed a clear correlation with increasing heat flux resulting in an increased probability for particle production. A correlation coefficient of $r^2 = 0.42$ is calculated for the 3 m level and coefficient of $r^2 = 0.92$

is observed for the 22 m level. The highest probability is observed for a positive heat flux while the lowest probability is observed for a negative heat flux. Since wind speed may influence the vertical exchange intensity of the heat flux, one can remove this influence by dividing the heat flux by u_* . In doing so, the correlation coefficient at the 3 m level increases to $r^2 = 0.67$ while the correlation at 22 m remains unchanged.

[28] No strong relationship was seen between particle production probability and water vapor flux (only available for the 3 m level); however, water vapor flux is also expected to be influenced by mean wind speed over the ocean, more so than heat flux. Removing the wind speed influence on water vapor flux by dividing the flux by u_* results in a good correlation ($r^2 = 0.56$) between particle production probability and normalized water vapor flux (Figure 10). Finally, the relationship between particle

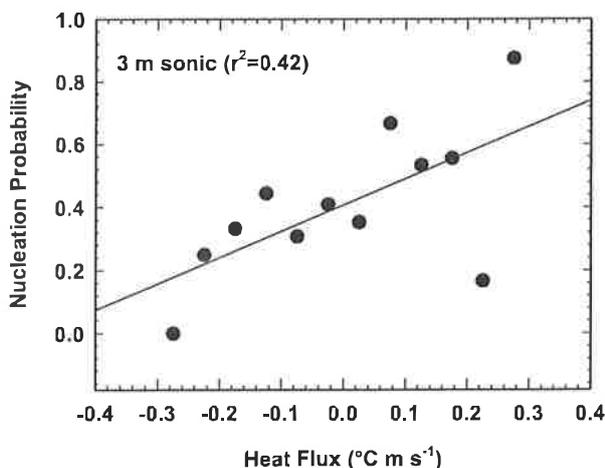


Figure 8. Nucleation probability as a function of kinematic heat flux at the 3 m level.

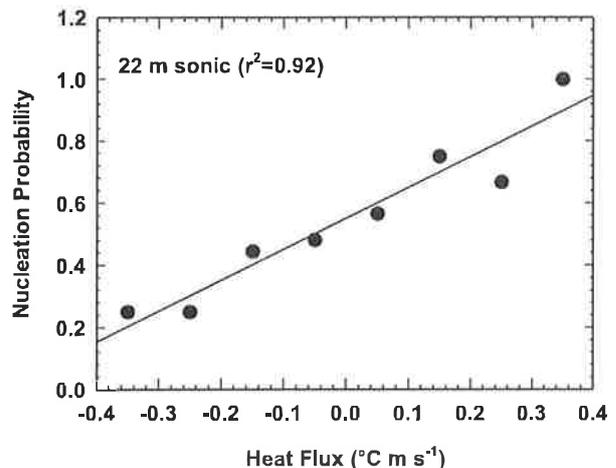


Figure 9. Nucleation probability as a function of kinematic heat flux at the 22 m level.

production probability and relative humidity is shown in Figure 11 for the 3 m level, where a correlation coefficient of $r^2 = 0.97$ is seen. A particle production probability of 1 is predicted for relative humidity between 55 and 65, while a particle production probability of 0 was observed for relative humidity of 90–95%.

6. Discussion and Conclusions

[29] Synoptic weather conditions (including air temperature and wind speed) and air mass origin do not appear to have any influence on the production of particles in the coastal zone. In terms of large-scale meteorological processes, for particle production to occur, the air must have recently advected over exposed shore regions during low tide conditions and in the presence of solar radiation. Analysis of the probability of particle production indicates that there is no clear relation with vertical wind velocity, and that particle production is not influenced by temperature variances. On the other hand, the particle production events are significantly influenced by enhanced, and particularly positive, heat fluxes concomitant with reduced water vapor fluxes over the exposed tidal area. These conditions correspond to the drying out of the tidal region as the tide recedes. As the residual water on the shore surface evaporates, water flux reduces and the available water to evaporate becomes smaller. Further, once the bulk of the water is evaporated, the heat flux is increased significantly since no more heat is required for the evaporation process. As the water evaporates, the shore biota are in a state of drying and are expected to be stressed due to the lack of water along with more direct exposure to direct solar radiation and consequent warming of the biota. The stress on the biota is known to promote increased emissions of biogenic vapors such as halocarbon species [Carpenter *et al.*, 1999, 2000; Laturus *et al.*, 2000]. Along with enhanced heat flux, there would be an expected enhancement of the vertical exchange of biogenic gases resulting from the increased stress on the biota in the drier environment and under direct solar radiation. It may also be possible that the biogenic vapor flux is also enhanced by the

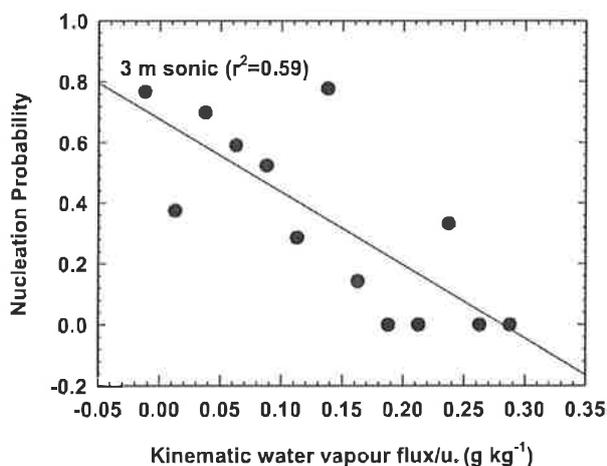


Figure 10. Nucleation probability as a function of kinematic water vapor flux (normalized for wind speed influences).

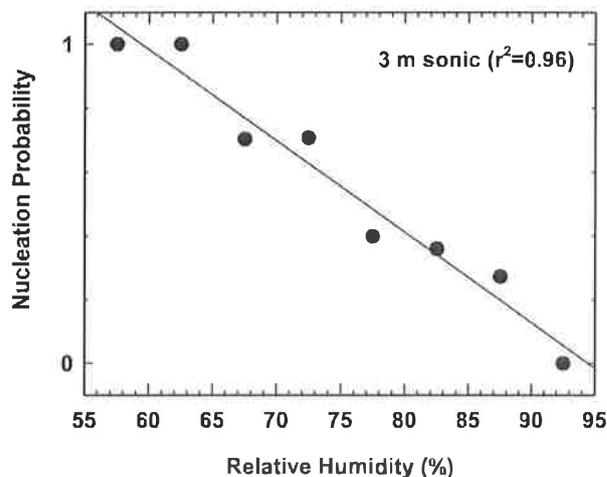


Figure 11. Nucleation probability as a function of relative humidity at the 3 m level.

added buoyancy associated with the enhance heat flux. While it is difficult to conclusively state that particle production is driven by these micrometeorological processes, the results presented here suggest, at least, the meteorological fluxes can be used as indicators, or predictors, of when new particle production is most likely to occur.

[30] The increased probability for particle production at lower water vapor fluxes and lower humidities indicates that enhanced water vapor concentration does not promote nucleation and/or growth of the new particles. This is not what is predicted for the nucleation of sulphuric acid and water vapor suggesting that another nucleation mechanism may be dominant in this environment. While theoretical predictions of ternary nucleation of sulphuric acid-water-ammonia suggest that nucleation is possible in this environment given the environmental conditions [Kulmala *et al.*, 2002], the negative correlation between particle production probability and water vapor flux and relative humidity provides some support for the production of new particles through the self-nucleation of iodine oxides proposed by Hoffmann *et al.* [2001].

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