

Submicron sea spray fluxes

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[1] Eddy covariance aerosol flux measurements were conducted at the Mace Head coastal station in the North East Atlantic. Footprint and micrometeorological analysis under clean marine air mass conditions indicated that fluxes representative of open ocean conditions could be derived during high tide conditions and an oceanic fetch. Sea-spray fluxes were derived for total particle sizes larger than 10 nm and total particle sizes larger than 100 nm (i.e. covering the Aitken and Accumulation mode). The source fluxes (F) were found to be strongly correlated with both wind speed (U) and friction velocity (u^*), following, by convention, an exponential relationship ($\log F = aU + c$) relationship. Comparison of source fluxes at sizes larger than 10 nm and larger than 100 nm demonstrates that approximately 50% of the number flux can be attributed to the accumulation mode and 50% to the Aitken mode. At 10 ms^{-1} wind speeds, the total primary marine aerosol flux is of the order of $2 \times 10^6 \text{ m}^{-2} \text{ s}^{-1}$, increasing to $20 \times 10^6 \text{ m}^{-2} \text{ s}^{-1}$ at 20 ms^{-1} . **Citation:** Geever, M., C. D. O'Dowd, S. van Ekeren, R. Flanagan, D. E. Nilsson, G. de Leeuw, and Ü. Rannik (2005), Submicron sea spray fluxes, *Geophys. Res. Lett.*, 32, L15810, doi:10.1029/2005GL023081.

1. Introduction

[2] Marine aerosols contribute significantly to the global aerosol field given the 70% coverage of the Earth's surface. The potential importance of marine aerosols to the climate system has been highlighted by Shaw [1983] and Charlson *et al.* [1987] where they implicated sulphate marine aerosols in a climate feedback system. They postulated that small changes in the availability of sulphate cloud condensation nuclei would result in increased cloud albedo, thereby contributing to the indirect aerosol effect.

[3] While much of the attention had focused on the sulphur cycle and sulphate aerosols, there is clear evidence that sea-spray aerosol contributes significantly to the marine aerosol. The work of Dinger *et al.* [1972] reported a significant fraction of sea-salt CCN at cloud base over the Atlantic Ocean and later work by O'Dowd and Smith [1993]

corroborated the existence of submicron sea-salt during experiments over the North East Atlantic and reported the first wind-speed relationship for accumulation mode sea-salt. Studies on the wind-speed - sea-salt relationship led Latham and Smith [1990] to postulate that sea-salt aerosol could also be involved in a cloud-climate feedback process if global wind speeds were to increase with global warming.

[4] More recent studies also showed that sea-spray aerosol can not only contain inorganic sea-salt, but also can contain significant, if not dominant organic matter components [O'Dowd *et al.*, 2004]. O'Dowd *et al.* [2004] found that the organic fraction in marine aerosol was strongly correlated with organic matter in the oceanic surface layer using chlorophyll-*a* as a proxy for organic matter and biological activity. These studies highlight the importance of quantifying the different components of the marine aerosol in terms of their micro-physics and chemical properties.

[5] The most commonly used flux scheme is that of Monahan [1986], however, this scheme strictly only applies to particles in the range to 0.8–10 μm , whereas current model efforts require extension fully into the accumulation mode and even into the Aitken mode [Vignati *et al.*, 2001; Gong, 2003]. In addition, the most recent review of marine aerosol fluxes have highlighted orders of magnitude in the difference between different flux estimates [Andreas, 2002], although the most recent estimates are converging to within one order of magnitude or better.

[6] In an effort to address this gap, Nilsson *et al.* [2001] conducted pioneering eddy-correlation measurements of sea-spray aerosol in terms of total particle concentration greater than 14 nm. These measurements, confined to Arctic water, suggested a significant sub-micron sea-spray flux, although it was not possible to distinguish the fraction of the flux contributing to the Aitken mode (10–100 nm) or the accumulation mode (100–1000 nm). Other studies addressing this gap are summarised by Schulz *et al.* [2004].

[7] In this study, we present the first eddy-covariance aerosol flux measurements over temperate oceanic waters of the North Atlantic.

2. Experiment and Data Analysis

2.1. Sampling Location

[8] The experimental location for the flux measurements study was the Mace Head atmospheric research station. The station is located on the west coast of Ireland (53°20'N, 09°54'W) and is regularly subjected to clean north-east Atlantic air masses. The 22 m tower was chosen as the host platform for the flux package as this was the highest point nearest to the ocean. The tidal region itself is very inhomogeneous and the land-sea transition extends from approximately 80 m from the base of the tower at high tide

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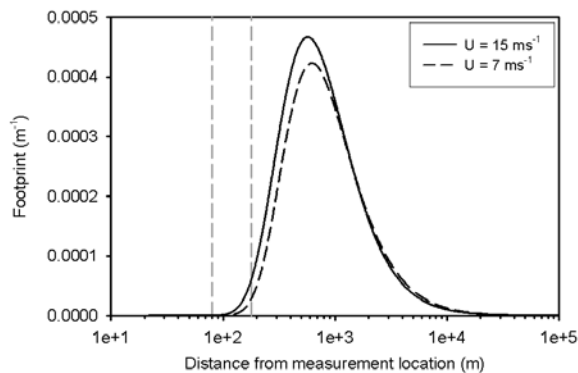


Figure 1. Flux measurement footprint derived for 22 m sampling tower at Mace Head for high wind speeds (solid curve) and moderate wind speeds (dashed curve). The vertical dashed lines mark the bounds of the low tide and high tide region.

to about 180 m at low tide. A full description of the station characteristics and measurement capability is summarised by Jennings *et al.* [2003]. The measurements were undertaken over a 4 week period in June and July 1992.

2.2. Instrumentation

[9] The flux package comprised a Solent sonic anemometer (Gill Windmaster Pro) to provide 3-D wind fields at 10 Hz, a TSI Condensation Particle Counter (CPC) 3760 covering total particle concentration from 10 nm to 1 micron, and a Particle Measurement Systems ASAP-X optical particle counter providing total particle concentration at sizes from 100 nm to 1 micron. The aerosol instruments were calibrated and regularly validated through comparison with SMPS spectrometers during the campaign. The three instruments were interfaced to a PC/104 Prometheus data logger which was in turn networked to a central logging computer. The sonic anemometer was mounted 2 meters out from the sea-facing side of the 22 m tower and a turbulent flow [Buzorius *et al.*, 1998] aerosol sampling inlet, 2.5 cm in diameter, was co-located at the base of the sonic anemometer, drawing air into the particle counting instrument housing located at the top platform of the tower.

2.3. Data Analysis

[10] For the calculation of fluxes, the raw data underwent initial filtering and inspection so that spikes and other anomalies could be removed. The covariance of two time series is the average product of the departures of the two corresponding variables from their respective means. The eddy-covariance technique is based on the assumption that conditions are steady (no low frequency trends present in the data) so it is necessary to de-trend the data by using departures from a short-term or a suitably chosen running mean. For this analysis, a half-hour running mean was selected and all variances and covariances were calculated from this mean, which yielded a single value for aerosol flux every half hour. Coordinate rotations, which result in zero vertical and transverse mean wind speeds, were applied to the variances and covariances from the half-hour means before the fluxes were calculated. A lag time correction was

then applied to take into account the aerosol residence time from the sample inlet to the aerosol detectors. This was achieved by maximising the correlation between the time-stamp and particle number concentration matrices and noting the time shift required to obtain this. The time lag thus calculated was 1 second. The vertical fluxes of aerosols were obtained from the covariance of vertical wind with aerosol number concentration. A more detailed description of the analysis procedures are given by Aubinet *et al.* [2000] and Nilsson *et al.* [2001].

3. Results

3.1. Micrometeorology and Flux Footprint

[11] The footprint for the measurements at the 22 m tower was evaluated using the analytical footprint model Horst and Weil [1992]. Micrometeorological data recorded by the Mace Head flux system were used as inputs. The thermodynamic state of the boundary layer throughout the period was mostly characterised by near neutral conditions. For the purpose of illustration, different wind speed regimes were chosen and Figure 1 shows a plot of the calculated footprint (m^{-1}) plotted as a function of the distance from the measurement location for two cases: (1) moderately high (15 ms^{-1}) wind speed (solid curve); and (2) moderately low (7 ms^{-1}) wind speed (dashed curve). Also marked on the plots with the vertical dashed lines are the approximate limits of the high and low tide levels from about 80 m at high tide to about 180 m at low tide. In both cases, the peak of the footprint representing the most likely source region for the measurements is at a distance of about 500 m from the tower location and significant contributions can be found at distances up to 1–10 km from the tower.

[12] The C_D measured in the current study during on-shore flow and high tide is presented as a function of wind speed in Figure 2a. A least squares fit provides the following relation: $C_D \times 10^3 = 0.088 U_{22} + 0.48$. Comparison of these numbers with those derived from other measurements [Geernaert, 1990] show that the wind speed dependence is a bit higher than over the mid North Atlantic which is typically 0.06 to 0.07. However, it is smaller than over the coastal North Sea (0.108 ± 0.003 at Meetpost Noordwijk in water depth of 18 m) and similar to results obtained over the

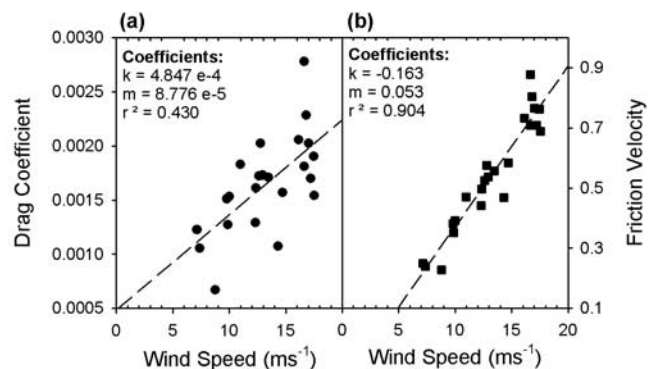


Figure 2. Relationship between (a) drag coefficient (C_D) and wind speed and (b) friction velocity (u^*) and wind speed for high tide conditions.

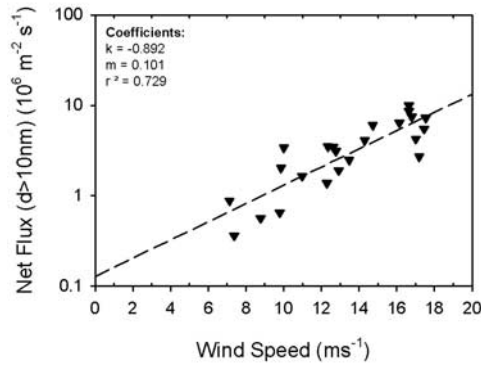


Figure 3. Net particle flux ($d > 10$ nm) for high tide conditions.

North Sea in deeper water of 30 m (0.089 ± 0.003) [Smith *et al.*, 1992].

[13] The values of C_D measured on the 22 m tower in the present study, which were typically less than 2×10^{-3} during high tide conditions in wind speeds up to 18 ms^{-1} (see Figure 2a) and thus support the conclusions from these previous measurements where Kunz and de Leeuw [2000] also concluded that measurements from the 22 m level were representative of open-water conditions. As discussed in section 3, such values can be regarded as typical for deep water conditions. Further analysis of u^* led to a similar conclusion as shown in Figure 2b. u^* was highly correlated to U_{22} during high tide conditions with $r^2 = 0.9$ while under low tide conditions, the correlation reduced to 0.75.

[14] From this analysis, it is plausible to assume that the tidal zone has relatively little influence, in terms of area contribution, on the measurements even at low tide and that at high tide the footprint is entirely oceanic. However, it is noted that the sea spray flux per unit area in the surf zone may be an order of magnitude higher than that over the open ocean [de Leeuw *et al.*, 2000] and hence to minimize the influence of such effects, only high tide conditions were used in the analysis.

3.2. Aerosol Fluxes

[15] Data were additionally screened for wind sector and to periods where the water level was greater than 70% of difference between the maximum water mark above the mean water mark. Using the remaining data, the net flux

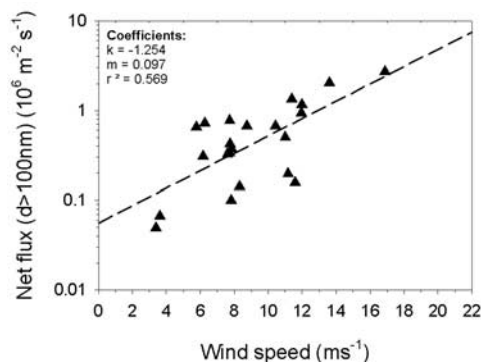


Figure 4. Net particle flux ($d > 100$ nm) for high tide conditions.

Table 1. Log-Linear Fit Parameters for Total Particle Number Concentration Fluxes as Functions of Wind Speed, U , and Friction Velocity, u^*

d > 10 nm	d > 100 nm
<i>Net Fluxes</i>	
Log(F) = 0.10U − 0.89 (r ² = 0.73)	Log (F) = 0.097U − 1.25 (r ² = 0.57)
Log (F) = 1.80 u* − 0.54 (r ² = 0.74)	Log(F) = 1.47 u* − 1.01 (r ² = 0.65)
<i>Source Fluxes</i>	
Log(F) = 0.099U − 0.73 (r ² = 0.81)	Log(F) = 0.109U − 1.19 (r ² = 0.65)
Log(F) = 1.63 u* − 0.28 (r ² = 0.60)	Log(F) = 1.59 u* − 0.94 (r ² = 0.62)

(i.e. the sum of the source flux and the deposition flux) was calculated and examined as a function of wind speed. The relationship between wind speed and net flux for total particle concentration larger than 10 nm is shown in Figure 3 while Figure 4 shows a similar plot for particles larger than 100 nm.

[16] A strong relationship between particle flux and wind speed was seen in both size ranges. For particle sizes >10 nm a correlation coefficient of $r^2 = 0.73$ was found for a log-linear relationship and for sizes >100 nm, $r^2 = 0.57$. By contrast, a very low correlation coefficient between net flux ($d > 10$ nm) and wind speed of $r^2 = 0.024$ was found at low tide. It should be noted that at the moderate-to-high high wind speeds ($>10 \text{ ms}^{-1}$) there is little difference between the low tide and high tide fluxes, however, at low wind speeds, the difference is significant: as wind speed increases, there is less difference between whitecap coverage over ocean and surf zone. During high tide, peak fluxes at 18 ms^{-1} were of the order of $10 \times 10^6 \text{ m}^{-2} \text{ s}^{-1}$, decreasing to $0.2\text{--}1 \times 10^6 \text{ m}^{-2} \text{ s}^{-1}$ at 7 ms^{-1} . The relationship was found to be in the form of $\text{Log } F (\text{m}^2 \text{ s}^{-1}) = 0.10 U (\text{m s}^{-1}) - 0.89$ where U is the mean horizontal wind speed at 22 m.

[17] The net flux is a measure of the source flux at the measurement height and the deposition flux at that same measurement height [Hoppel *et al.*, 2005] and consequently, to derive source fluxes, we have to calculate deposition fluxes for each flux period and add this to the net flux to arrive at the source flux [Nilsson *et al.*, 2001]. In calculating the deposition flux, the model of Schack *et al.* [1985] was applied to size distributions measured over the 10 nm to 1 micron size range for measured stabilities and meteorological parameters during each 30 minute averaging period. These deposition fluxes exhibited some wind speed dependence and typically accounted for a 20–30% correction to the net fluxes. After accounting for the deposition flux, the source flux, as a function of wind speed, was examined and a relationship of the form $\text{Log } F (\text{m}^2 \text{ s}^{-1}) = 0.099 U (\text{m s}^{-1}) - 0.73$ was observed for particles sizes >10 nm. This relationship possessed a correlation coefficient of $r^2 = 0.81$ and has a similar slope to that for the net fluxes. Similar relationships were obtained between the source flux of particles >100 nm and wind speed. Often the fluxes are parameterised in term of the friction velocity u^* which in neutral conditions is linearly related to the wind speed. The advantage of using u^* is that the effects of thermal stability are eliminated from the parameteriza-

tion. Results from relationships between particles in both size ranges, wind speed at 22 m (U_{22}) and friction velocity, u^* are summarised in Table 1. It should be noted that the difference between the 10 m wind speed and the 22 m wind speed is of the order of a few percent and therefore the relationships are left in terms of U_{22} .

[18] The ratio between the total source fluxes from 10–1000 nm and from 100–1000 nm was found to decrease from 2.8 at 2 ms^{-1} to 1.8 at 20 ms^{-1} ; however this is likely due to the relatively poor overlap in the two data sets for lower wind speed values whereas there is better overlap at higher end of the range and the ratio is close to 2. These measurements represent the first pseudo-size-segregated marine aerosol fluxes for submicron particles. The key new result is that there is a significant flux of particles in the 10–100 nm size range, in agreement with the laboratory experiments by *Mårtensson et al.* [2003]. At 10 ms^{-1} wind speeds, the total sub-micron primary marine aerosol flux is of the order of $2 \times 10^6 \text{ m}^{-2} \text{ s}^{-1}$, increasing to $20 \times 10^6 \text{ m}^{-2} \text{ s}^{-1}$ at 20 ms^{-1} . Fluxes of this magnitude can contribute significantly to the total background particle concentration over oceanic regions.

4. Conclusions

[19] Eddy correlation measurements of aerosol fluxes, for sizes between 10 nm and 1000 nm, over the North Atlantic show a strong correlation with wind speed (net flux: $\text{Log } F(\text{m}^2 \text{ s}^{-1}) = 0.10U (\text{m s}^{-1}) - 0.89$, $r^2 = 0.73$; source flux $\text{Log } F(\text{m}^2 \text{ s}^{-1}) = 0.099U (\text{m s}^{-1}) - 0.73$, $r^2 = 0.81$). These measurements represent the first pseudo-size-segregated aerosol flux measurements indicating a significant contribution in the Aitken mode (50% of the sub-micron fluxes). Fluxes of this magnitude can readily contribute significantly to background marine aerosol concentrations and must be considered as important as secondary formation rates over the oceans. Further work is required to develop a sub-micron sea-spray source function which also incorporates the processes that lead to the changes in micro-physical and chemical properties of bubble-mediated aerosol production driven by seasonality changes. Such work should include temperature effects and the effect of adsorbed organic matter in the ocean surface micro-layer both of which could influence the size-resolved fluxes.

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References

- Andreas, E. L. (2002), A review of the sea spray generation function for the open ocean, in *Atmosphere-Ocean Interactions*, vol. 1, edited by W. A. Perrie, pp. 1–46, WIT Press, Southampton, UK.
- Aubinet, M., et al. (2000), Estimates of the annual net carbon and water exchange of European forests: The EUROFLUX methodology, *Adv. Ecol. Res.*, **30**, 113–175.
- Buzorius, G., Ü. Rannik, J. M. Mäkelä, T. Vesala, and M. Kulmala (1998), Vertical aerosol particle fluxes measured by eddy covariance technique using condensational particle counter, *J. Aerosol Sci.*, **29**, 157–171.
- Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren (1987), Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate, *Nature*, **326**, 655–661.
- De Leeuw, G., F. P. Neele, M. Hill, M. H. Smith, and E. Vignati (2000), Sea spray aerosol production by waves breaking in the surf zone, *J. Geophys. Res.*, **105**, 29,397–29,409.
- Dinger, J. E., H. B. Howell, and T. A. Wojciechowski (1972), On the source and composition of cloud nuclei in a subsident air mass over the North Atlantic, *J. Atmos. Sci.*, **27**, 791–797.
- Geernaert, G. L. (1990), Bulk parameterizations for the wind stress and heat fluxes, in *Surface Waves and Fluxes*, vol. I, edited by G. L. Geernaert and W. J. Plant, pp. 91–172, Springer, New York.
- Gong, S. L. (2003), A parameterization of sea-salt aerosol source function for sub- and super-micron particles, *Global Biogeochem. Cycles*, **17**(4), 1097, doi:10.1029/2003GB002079.
- Hoppel, W. A., P. F. Caffrey, and G. M. Frick (2005), Particle deposition on water: Surface source versus upwind source, *J. Geophys. Res.*, **110**, D10206, doi:10.1029/2004JD005148.
- Horst, T., and J. Weil (1992), Footprint estimation for scalar flux measurements in the atmospheric surface layer, *Boundary Layer Meteorol.*, **59**, 279–296.
- Jennings, S. G., C. Kleefeld, C. D. O'Dowd, C. Junker, T. Gerard Spain, P. O'Brien, A. F. Roddy, and T. C. O'Connor (2003), Mace Head Atmospheric Research Station—Characterization of aerosol radiative parameters, *Boreal Environ. Res.*, **8**, 303–314.
- Kunz, G. J., and G. de Leeuw (2000), Micrometeorological characterisation of the Mace Head field station during PARFORCE, in *New Particle Formation and Fate in the Coastal Environment (PARFORCE)*, Rep. Ser. Aerosol Sci., vol. 48, edited by C. O'Dowd and K. Hämeri, pp. 55–62, Finn. Assoc. Aerosol Res., Helsinki.
- Latham, J., and M. H. Smith (1990), Effect on global warming of wind-dependent aerosol generation at the ocean surface, *Nature*, **347**, 372–373.
- Mårtensson, E. M., E. D. Nilsson, G. De Leeuw, L. H. Cohen, and H. C. Hansson (2003), Laboratory simulations and parameterization of the primary marine aerosol production, *J. Geophys. Res.*, **108**(D9), 4297, doi:10.1029/2002JD002263.
- Monahan, E. C. (1986), The ocean as a source of atmospheric particles, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Menard, pp. 129–163, Springer, New York.
- Nilsson, E. D., Ü. Rannik, E. Swietlicki, C. Leck, P. P. Aalto, J. Zhou, and M. Norman (2001), Turbulent aerosol fluxes over the Arctic Ocean: 2. Wind driver sources from the sea, *J. Geophys. Res.*, **106**, 32,139–32,154.
- O'Dowd, C. D., and M. H. Smith (1993), Physico-chemical properties of aerosol over the northeast Atlantic: Evidence for wind speed related sub-micron sea-salt aerosol production, *J. Geophys. Res.*, **98**, 1137–1149.
- O'Dowd, C. D., M. C. Facchini, F. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y. J. Yoon, and J. P. Putaud (2004), Biogenically-driven organic contribution to marine aerosol, *Nature*, **431**, 676–680, doi:10.1038/nature02959.
- Schack, C. J., S. E. Pratsinis, and S. K. Friedlander (1985), A general correlation for deposition of suspended particles from turbulent gases to completely rough surfaces, *Atmos. Environ.*, **19**, 953–960.
- Schulz, M., G. de Leeuw, and Y. Balkanski (2004), Sea-salt aerosol source functions and emissions, in *Emissions of Atmospheric Trace Compounds*, edited by C. Granier, P. Artaxo, and C. Reeves, pp. 333–359, Springer, New York.
- Shaw, G. (1983), Bio-controlled thermostasis involving the sulfur cycle, *Clim. Change*, **5**, 297–303.
- Smith, S. D., et al. (1992), Sea surface wind stress and drag coefficients: The HEXOS results, *Boundary Layer Meteorol.*, **60**, 109–142.
- Vignati, E., G. de Leeuw, and R. Berkowicz (2001), Modeling coastal aerosol transport and effects of surf-produced aerosols on processes in the marine atmospheric boundary layer, *J. Geophys. Res.*, **106**, 20,225–20,238.
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