

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# Do anthropogenic or coastal aerosol sources impact on a clean marine aerosol signature at Mace Head?

C. O'Dowd<sup>1</sup>, D. Ceburnis<sup>1</sup>, J. Ovadnevaite<sup>1</sup>, M. Rinaldi<sup>2</sup>, and M. C. Facchini<sup>2</sup>

<sup>1</sup>School of Physics and Centre for Climate and Air Pollution Studies, Ryan Institute, National University of Ireland Galway, University Road, Galway, Ireland

<sup>2</sup>Istituto di Scienze dell'Atmosfera e del Clima, Consiglio Nazionale delle Ricerche, Bologna, Italy

Received: 10 February 2013 – Accepted: 14 February 2013 – Published: 20 March 2013

Correspondence to: C. O'Dowd (colin.odowd@nuigalway.ie)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Atmospheric aerosols have been sampled and characterised at the Mace Head North East (N.E.) Atlantic atmospheric research station since 1958, with many interesting phenomena being discovered. However, with the range of new discoveries and scientific advances, there has been a range of concomitant criticisms challenging the representativeness of aerosol sampled at the station to that of aerosol over the open ocean. Two recurring criticisms relate to the lack of representativeness due to enhanced coastal sources, thereby leading to artificially high values to aerosol parameters, and to the influence of long-range transport of anthropogenic aerosol and its potential dominance over, or drowning-out of, a natural marine aerosol signal. Here we review the results of previous experimental studies into marine aerosols over the N.E. Atlantic and at Mace Head with the aim of evaluating their representativeness relative to that of an open ocean aerosol with negligible anthropogenic influence. Particular focus is given to organic matter (OM) aerosol. In summary, no correlation was found between OM and black carbon (BC) either at BC levels of 0–15 or 15–50 ng m<sup>-3</sup>, suggesting that OM concentrations up to peak values of 3.8 µg m<sup>-3</sup> are predominantly natural in origin. Sophisticated carbon isotope analysis and aerosol mass spectral fingerprinting corroborate the natural source of OM with 80 % biogenic source apportionment being observed for general clean air conditions, rising to 98 % during specific primary marine organic plumes when peak concentrations > 3 µg m<sup>-3</sup> are observed. A range of other experiments are discussed which corroborate the dominance of a marine signal under Mace Head clean air criteria along. Further, analysis of a series of experiments conducted at Mace Head conclude that negligible coastal, surf zone, or tidal effects are discernible in the submicron size range for sampling heights of 7 m and above. The Mace Head clean air criteria ensures anthropogenic and coastal effects are sufficiently minimised so as to guarantee a dominant, if not at times, an overwhelming natural marine aerosol signal.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 1 Introduction

The marine aerosol is perhaps the most important natural system globally in terms of climate effects. This is so because the ocean covers 70 % of the earth's surface and marine aerosol haze and cloud layers are the most effective reflecting layers given that they overly a dark ocean surface (Charlson et al., 1987; Slingo, 1990). There are two generic marine aerosol types (O'Dowd and de Leeuw, 2007; de Leeuw et al., 2011): primary and secondary. Primary marine aerosol was initially considered to be predominantly sea-salt dynamically produced by wind stress interaction at the ocean surface; however, later it became evident that primary marine aerosol was better described as sea-spray – a combination of sea-salt and enriched primary organic matter (POM) resulting biological processes at the ocean surface (O'Dowd et al., 2004).

The secondary aerosol type (Facchini et al., 2008a) comprises a range of species produced in the gas phase or from gas phase processes and can be categorised as volatile organic compound (VOC) oxidation products in the condensed phase (Rinaldi et al., 2011), or non-sea-salt (nss) sulphate produced from the oxidation of dimethyl sulphide (DMS), or a hybrid organo-sulphur species such as methanesulfonic acid (MSA), also a DMS oxidation product, can also be present in significant quantities. Organo-nitrogen, in the form of dimethyl amine (DMA) is also present to a lesser degree (Facchini et al., 2008a). More often than not, secondary inorganic aerosol such as nss-sulphate dominates over secondary organic aerosol (SOA).

In pristine environments, if it can be argued that they even exist, it can be quite a challenge to characterise the marine aerosol since the primary aerosol depends on dynamics producing the spray, biological activity which determines the organic matter enrichment, and oxidant availability which determines the degree of processing of POM to SOA-like OM in the spray itself – all processes which are highly variable in time and space. Similarly, biological activity, sea water temperature, sea-to-air transfer, wave dynamics, cloudiness, photolysis rates etc. all influence the concentration of marine SOA. The problem is further compounded by the fact that basic organic, sulphate

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and nitrates analytical techniques cannot source-apportion these chemical species and thus, cannot conclusively elucidate whether or not they are natural or anthropogenic in origin.

The challenge is to understand as many of the key marine aerosol processes driving formation, transformation and climate impacts but how is this to be achieved? Intermittent and ad-hoc cruises are used to access so-called remote and pristine regions; however, their spatial and temporal snapshots are limited and only provide glimpses of the complete picture, often missing high wind speed events or regions of high biological productivity. Aircraft missions, while excellent for providing vertical structure information, have even greater limitations, particularly in the context of long temporal datasets. Coastal stations provide a solution to the temporal sampling problem, although these are limited to a fixed spatial location but the question arises as to whether or not there are local sources contaminating the “open ocean marine” signal and/or how pristine is the apparent open ocean marine aerosol?

The problem is that wherever sampling of marine aerosol is conducted, particularly if the focus is on the submicron fraction, there exists significant challenges relating to contamination whether it be anthropogenic or related to coastal topographical issues. If such contamination exists, do we “throw the baby out with the bath water” or is there an acceptable level of contamination which will still allow the elucidation and quantification of natural aerosol processes? This is, of course, a subjective question – we know that there is long range pollution transport to Antarctica as seen in the black carbon records. Does this mean that Antarctica is not a useful location to study natural aerosol? Clearly, the answer is no, it depends on whether or not the natural signal is overwhelmed by the contaminated signal! What is an acceptable contamination threshold – 1 %, 5 %, 10 %, 25 %? If we contrast the North East Atlantic marine aerosol entering into Europe in the Mace Head Region, black carbon mass is higher than that in Antarctica although it is also perhaps one of the most biologically-rich and stormiest oceans there is. Again, is there a sufficient natural open ocean signal to elucidate key processes or should such experiments be abandoned? This study reviews some of the key experiments

## Mace Head aerosol

C. O’Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



conducted at Mace Head and evaluates how they have been interpreted, or in some cases, misinterpreted, with the aim of elucidating the conditions acceptable for non-contaminated marine aerosol research.

## 2 The Mace Head facility

5 The Mace Head Atmospheric Research Station is located in Connemara, County Galway on the Atlantic Ocean coastline of Ireland at 53°19' N, 9°53' W and offers a clean sector from 190° west through to 300° (see Fig. 1). Meteorological records show that on average, over 60 % of the air masses arrive at the station in the clean sector (Jennings et al., 2003; O'Connor et al., 2008). Air is sampled from a 10 m height tower and a 22 m tower, both situated ~ 100 m from the shore-line and ~ 50 m from high water (http://www.macehead.org). The shoreline is relatively inhomogeneous and rocky with a slope of ~ 4°. The 22 m tower is situated between two 8 m high “shore” laboratories (Fig. 1) while the 10 m tower is located adjacent to the north gable of the more northerly aerosol laboratory. The southerly shore laboratory hosts the gas sampling experiments. Also shown in Fig. 1 is the whitecap and surfzone field under moderately windy conditions.

## 3 Interpretation of previous results

### 3.1 Aerosol characterisation under wind-sector controlled sampling

20 In the absence of highly sophisticated and expensive analytical techniques capable of directly apportioning a particular aerosol chemical species to a particular source, there are a number of real-time and post analysis procedures used to try to distinguish between pristine, or baseline, marine aerosol and that which is significantly influenced by anthropogenic sources. These filtering approaches range from wind-sector controlled sampling in real-time, sometimes augmented by parallel total particle concentration

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



control, to post analysis of air mass back-trajectories, BC mass concentrations and/or correlations between the concentration of the species being measured and an anthropogenic tracer such as BC or CO and are discussed in the following sections.

Some of the first chemical mass measurements undertaken at Mace Head were from August 1988 to August 1990 by Savoie et al. (2002). The 22 m tower was used for the aerosol filter sampling. The aerosol sampler was connected to a clean-sector controller which was designed to capture clean marine onshore winds; however, nss-sulphate mass concentrations of up to  $10\text{--}20\ \mu\text{g m}^{-3}$  were reported, along with nitrate mass concentrations exceeding  $10\ \mu\text{g m}^{-3}$ . Clearly, these concentrations cannot be regarded as representative of clean marine air advecting in off the Atlantic. Can these results be interpreted, as concluded by Savoie et al. (2002), as the Mace Head marine sector aerosol composition being significantly impacted by anthropogenic emissions and that on average 85–90 % of the nss-sulphate in marine flow at Mace Head as originating from anthropogenic sources? Well, on face value, this indeed could be the conclusion one arrives at; however, closer examination of the experimental and sampling criteria reveals a different conclusion.

While the aforementioned experimental studies were pioneering and revealing, the experimental design of the sampling component of the study was not completely fit-for-purpose in that the criterion used to exclude polluted European air masses, which can recirculate into the clean sector, was insufficient. In contrast, subsequent studies by O'Dowd et al. (2004), Cavalli et al. (2004), Yoon et al. (2007), and Ceburnis et al. (2011) used a more sophisticated set of sampling criteria: from 2001, the Mace Head active sector-controlled sampling system used both wind direction and total particle concentration as the primary controllers for sampling on-shore clean marine air masses. Total particle concentration was measured by a TSI 7610 condensation particle counter ( $D_{50} > 14\ \text{nm}$ ) and the counter was set to trigger sampling shutdown if particle counts exceeded  $700\ \text{particles cm}^{-3}$ . The real-time clean-air control criteria were evaluated in a post analysis quality control check during which additional criteria were deployed, namely: air mass back trajectories free from land contact for 96 hours

## Mace Head aerosol

C. O'Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



prior to arrival at Mace Head; and BC concentration measured by an Aethalometer (AE-16, Magee Scientific, single wavelength at 880 nm) did not exceed  $50 \text{ ng m}^{-3}$  as an upper limit. It should be noted that average BC mass concentrations would typically be less than half the upper limit for the real-time sampler controller criteria.

As it happened, in 2004, both the Savoie-type and the NUIG-type marine clean sector controllers were run in parallel and a scatterplot of their relationship is illustrated in Fig. 2 where each point represents nss-sulphate mass over a week long sample (noting that the actual sampling time depends both on the air mass and on the sampling criteria used). Although the Savoie system sampled Total Suspended Particulate matter (TSP), and the NUIG system used a Berner impactor with an upper size cut of 16 microns diameter, the systems effectively cover the same size range. The comparison indicates that the Savoie-type sector controller, more often than not, reports higher nss-sulphate masses compared to the NUIG system, often by a factor of 2 or 3. Also shown in Figure 2 are two contrasting cases from the 2004 dataset, visualised through air mass back trajectories: one in which only the Savoie-type controller sampled, and in fact, sampled only recirculating polluted air, as the particle concentration was above the clean-air threshold in the NUIG controller for the whole duration of the week; and the other where both systems successfully sampled clean air coherently throughout the week (i.e. due to the lack of circulating air in this case).

The measurements taken by Savoie et al. (2002) were conducted 25 yr ago, and while pioneering, it can only be concluded that the experimental design was not completely fit-for-purpose. Consequently, the results from that experiment simply cannot be used to define more recent experiments in terms of source apportionment. Apart from the experimental design, there are two additional reasons as to why great caution should be exercised when comparing more recent studies with the 25-yr old Savoie et al. (2002) study. First, the measurements of nss-sulphate by Savoie et al. (2002) related to bulk mass measurements where the nss-sulphate mass is derived from Na and sea-salt sulphate concentrations, both relatively very large numbers which result in large errors associated with derivation of the much smaller nss-sulphate mass. This

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

analytical uncertainty is particularly severe for bulk filter analysis compared to size segregated impactor sample analysis. Second, the emissions of anthropogenic SO<sub>2</sub> have reduced over the recent two decades and the annual average reduction in nss-sulphate mass at Mace Head has reduced by 70 % over the last ten years (O'Dowd et al., 2013).

While sulphate mass trends are not available at Mace Head for the 1990s, SO<sub>2</sub> trends from the nearby Valentia GAW station (www.emep.int) reveal an even greater reduction for the previous decade, suggesting that sulphate mass is likely to have reduced by ~ 80 % over the last 25 yr. The significant reduction in anthropogenic sulphur emissions is likely to explain the better agreement between the NUIG and Savoie-type 2004 data compared to the 1989–1990 Savoie et al. (2002) data. In summary, and based on an experimental set-up not completely appropriate for the task, high uncertainties associated with the analytical techniques, and the estimated ~ 80 % reduction in anthropogenic sulphate mass since the Savoie et al. (2002) study, it is simply not justified to claim, these days, that marine air masses arriving at Mace Head are 80–90 % influenced by anthropogenic aerosols.

### 3.2 Organic mass – black carbon relationships and ratios

Shank et al. (2012) evaluated the magnitudes and ratios of OM, BC and nss-sulphate over various regions in the Pacific in an attempt to elucidate the natural oceanic versus anthropogenic sources of OM. In our discussion, we focus only on the magnitudes of OM and the OM/BC ratio to determine origin of the OM since nss-sulphate can have both a natural marine and anthropogenic origin. It should be noted that Shank et al. (2012) present their AMS measurements of OM as being effectively the total OM aerosol mass based on an incorrect interpretation of O'Dowd et al. (2004) where they cite the study as having demonstrated that more than 90 % of the mass is within submicron sizes (i.e. the size range covered by their AMS). The correct interpretation of O'Dowd et al. (2004) is that while the percentage mass contribution of OM is up to 5 % in supermicron sizes, approximately 50 % of the total OM resides in the supermicron

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





sizes. Consequently, Shank et al. (2012) OM data refers mostly to only the submicron component.

During the Shank et al. (2012) TOA cruise, an OM mass concentration ranging from 0.07–0.17  $\mu\text{g m}^{-3}$  was found for screened clean marine air, and a VOCALS average of 0.07  $\mu\text{g m}^{-3}$  was encountered over Pacific waters. This is compared (Fig. 3) to off-line Berner-derived OM mass ranging from 0.16–0.54  $\mu\text{g m}^{-3}$  and 0.05–3  $\mu\text{g m}^{-3}$  for three years of on-line AMS data, increasing to  $> 3 \mu\text{g m}^{-3}$  in specific primary organic sea-spray plumes. Shank et al. (2012) conclude that OM was correlated to BC down to concentrations as low as 4.5  $\text{ng m}^{-3}$  and that most of the average OM observed in their Pacific studies was anthropogenic. Further, they also note that it may not be appropriate to fix a threshold OM mass concentration below which can be considered as non-perturbed marine air and suggest that a large fraction of OM mass observed at Mace Head is therefore anthropogenic. Figure 3 shows the scatter plots of OM versus BC for BC mass less than 15  $\text{ng m}^{-3}$  for N.E. Atlantic Aerosol sampled at Mace Head. What is observed is, more or less, no correlation between the two variables, even for extraordinary-high OM concentrations of  $> 3 \mu\text{g m}^{-3}$ , suggesting that the OM reported as marine OM at Mace Head is indeed clean marine OM aerosol.

Shank et al. (2012) also analysed the OM/BC ration and found a ratio of 10 in the remote Pacific and argued that even this approach was not robust given the large range of ratios encountered both in remote and clean marine environments as well as in polluted air. We expand the collection of OM/BC ratios (Table 1) to include additional southern hemisphere oceanic ratios along with our average Mace Head ratios. We find an OM/BC ratio of 60 for Amsterdam Island, 28 for Mace Head non-organic-plume events and 182 for primary organic sea-spray plumes detected at Mace Head. In fact, for hour average data, ratios approaching 1000 are seen. Such high OM/BC ratios over BC mass concentrations from 0–15  $\text{ng m}^{-3}$  provide compelling arguments supporting the case that OM observed under the clean air criteria at Mace Head is indeed natural marine OM.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

### 3.3 Chemical source-apportionment

The first attempt to source-apportion the secondary aerosol measured at Mace Head centred on sulphur isotope analysis conducted from 1993–1994 by McArdle et al. (1998). The study revealed a maximum biogenic sulphur contribution to total sulphur mass of 30 % in spring and summer and significantly less throughout the remainder of the year. In the latter study, samples were taken in all wind sectors. Results from this experiment could not elucidate the anthropogenic contamination contributing to the baseline marine signal since the analysis included all marine and continental air masses. A more recent attempt to source apportion sulphate aerosol over the Atlantic was undertaken by Lin et al. (2012), where they conducted east-west and north-south transects of the Atlantic. Of particular relevance to the discussion in this study is the east-west transect along 36° N, departing from midway along the USA east coast and arriving in Europe in the south of Portugal. The isotopic source apportionment of nss-sulphate demonstrates that close to the US east coast (e.g. sample 4 in Fig. 4, corresponding to -68.9° E 36.22° N), nss-sulphate is 70–80 % anthropogenic in origin, while as measurements extended out into the mid-N.E. Atlantic (sample 19 in Fig. 4, corresponding to -46.27° E 36.26° N), the natural contribution of sulphate peaked at > 90 %, although more generally in this region, it was nearer 75 %. For one third of the transect, the natural component was of the order of 70 %, reducing to 30–40 % as measurements were taken close to Europe. It should be noted that 36° N is considerably south of the Mace Head latitude and at the latitude of 36° N is prone to both continental outflow from the US, over the N.W. Atlantic, and Europe, over the N.E. Atlantic, much more so than the Mace Head latitude due to contrasting meteorological patterns. For example, the most common clean-marine air mass back trajectory arriving at Mace Head is that of a polar maritime air mass which enters into the Atlantic from Greenland and the sparsely-populated northern Canada, while along the 36° N line, air masses enter the N. Atlantic more from the polluted east coast US. Similarly, European continental outflow of pollution is more prevalent around southern Portugal, due to persistent high

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Mace Head aerosol

C. O'Dowd et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

pressure systems, compared to Mace Head which is more subject to eastwardly tracking cyclones. It was for precisely this reason on regular continental outflow that the ACE2 LAGRANGIAN experiments started in this region (Johnson et al., 2000).

Ceburnis et al. (2011) also used isotope analysis to source apportionment aerosol at Mace Head; however, their focus was on carbonaceous aerosols, using  $^{13}\text{C}$  and  $^{14}\text{C}$  isotopes to quantify anthropogenic, marine biogenic and terrestrial non-fossil carbon sources in submicron particles over the N.E. Atlantic. The contribution of marine biogenic carbon in marine air masses sampled by sector-controlled system was on average  $\sim 80\%$ , declining to  $32\%$  in non-marine air. In the marine samples, the remaining sources were  $14\%$  fossil fuel and  $7\%$  non-fossil fuel.

Decesari et al. (2011) investigated the origin of the water soluble organic carbon (WSOC) in marine aerosol samples collected at Mace Head using the sector-controlled system described above, through proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR). In order to disentangle the different components in the unresolved mixture that constitutes marine aerosol WSOC, they employed different factor analysis methods to extract spectral features on the basis of their variability between samples and interpreted them based on the correlation with known spectral profiles. In a five factor solution, the statistical analysis identified one factor which spectral profile showed the most prominent aromatic groups and exhibited the strongest correlation with typical spectra of WSOC in polluted environments. The contribution of this factor was clearly highest for the samples collected outside the clean sector, added to the dataset for comparison purposes, (Fig. 6) and was attributed to anthropogenic sources. On the other hand, all the other factors presented spectral features consistent with a marine biogenic origin. The contribution of anthropogenic sources, as identified by factor analysis, in the dataset investigated by Decesari et al. (2011) is  $17\%$  ( $\pm 13\%$ ), in a good agreement with the results of Ceburnis et al. (2011).

The aforementioned studies use low-temporal resolution sampling and subsequent off-line analysis. One drawback of such an approach is that maximum concentrations of particular aerosol species are smoothed out into long time-average values. With the

## Mace Head aerosol

C. O'Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



advent of on-line aerosol mass spectrometry, realtime source-apportionment of organic aerosol was made possible. Indeed, deployment of such measurement techniques by Ovadnevaite et al. (2011a, b) not only identified marine organic aerosol plumes with mass concentrations reaching  $3.8 \mu\text{g m}^{-3}$ , but also revealed a unique marine organic aerosol hydrocarbon fingerprint in contrast to anthropogenic hydrocarbons. It should be noted that the marine organic aerosol hydrocarbon pattern is dominated by  $\text{C}_n\text{H}_{2n-3}$  ( $m/z$  39, 53, 67, 81, etc.;  $\Delta = -2$ ) and missing the class  $\text{C}_n\text{H}_{2n+1}$  ( $m/z$  43, 57, 71, etc.;  $\Delta = 2$ ), which is indicative of refined hydrocarbons and predominant in the anthropogenic hydrocarbon mass spectrum. For the plume analysed, Fig. 7 illustrates that the air mass back trajectories advected over chlorophyll *a* rich and stormy waters upwind while Fig. 8 illustrates the unique mass spectral fingerprint associated with marine POM.

Further, this unique marine hydrocarbon species was highly correlated ( $R^2 > 0.98$ ) with an oxygenated hydrocarbon and suggested that approximately 98 % of the organic aerosol was associated with organic sea-spray, either partly oxidised or not oxidised at all. Such organic aerosol mass concentrations are not often encountered in marine air, and the concentrations rival those encountered in many urban regions; however, the mass spectral fingerprint and the observed OM/BC ratio of 182, combined with the clearly marine air mass back trajectories, suggest that these organics are extremely unlikely to be anthropogenic in origin.

### 3.4 Coastal sources and artefacts

Apart from anthropogenic contamination, coastal contamination is the other main potential threat to the marine representativeness of marine-sector aerosol sampled at Mace Head is that of coastal sources leading to artefacts, either in the form of enhanced surf-zone production of sea-spray and/or enhanced biological activity relative to open waters. In this section we review the evidence for minimal coastal surfzone artefacts along with minimal coastal organic aerosol production.

## Mace Head aerosol

C. O'Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



One of the first studies aimed at elucidating the contribution of surf-induced spray plumes, as opposed to breaking wave-induced spray plumes was that of Kunz et al. (2002) who deployed a horizontally and vertically scanning LIDAR at Mace Head to examine the production and dispersion of sea-spray plumes, demonstrating the formation and dispersion of surf-induced plumes from upwind rocks and islands, evolving to hundreds of meters in the vertical while transported a few kilometers horizontally from the source.

While the occurrence of surf-induced sea-spray plumes was clearly highlighted, the more complete and correct interpretation of the Kunz et al. (2002) study is that at wind speeds below whitecapping onset, surf-spray plumes from the upwind island are visible, given the absence of wave-breaking surf production and that these plumes are readily mixed and dispersed vertically. Further, as the wind speed approaches moderate levels of  $8 \text{ m s}^{-1}$ , the surf plumes produced upwind from Mace Head are increasingly indistinguishable from the breaking wave spray plumes. Given that wind speeds are almost exclusively above the whitecap threshold of  $4 \text{ m s}^{-1}$ , this would suggest minimal impact of upwind surf plumes on aerosol measured at Mace Head. Figure 9 illustrates the wind speed frequency distribution at Mace Head during the winter (3 month: December, January, February) and summer (3 month: June, July, August) periods. Also shown is a 3-day period of high wind speed about 200 km upwind from the MAP cruise during June 2006 and the simultaneous wind speed at Mace Head. What is evident from the frequency distributions is that in summer, the distribution has two peaks at 5 and  $8 \text{ m s}^{-1}$ ,  $\sim 15\%$  wind speed occurring below the whitecap threshold of  $4 \text{ m s}^{-1}$ . In winter, while also exhibiting a bi-modal structure, the primary peak is at  $9 \text{ m s}^{-1}$  and the secondary peak is at  $12 \text{ m s}^{-1}$ , with a 4% occurrence below the whitecap threshold. The up stream data during the MAP cruise illustrates the occurrence of broad  $20 \text{ m s}^{-1}$  frequency peak, extending to greater than  $30 \text{ m s}^{-1}$ , during a 2-day summer storm. The simultaneous wind speeds measured at Mace Head exhibit a narrow frequency distribution peak at  $14\text{--}15 \text{ m s}^{-1}$ . The point of this comparison is that very often there can be significantly higher winds off-shore which, potentially, could produce sufficient sea-

## Mace Head aerosol

C. O'Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



spray to dominate over that locally produced at Mace Head. Taking into account the wind speed frequency distribution in conjunction with the Kunz et al. (2002) analysis, one can only conclude minimal influence from off-shore breaking surf. Indeed, Kunz et al. (2002) themselves conclude “The influence of the background renders it difficult to quantify the effect of locally generated plumes on the concentrations at Mace Head in relation to wind direction and wind speed. In particular because during transport from the islands to the Mace Head station, vertical dispersion causes dilution of the primary aerosol, which brings the concentrations close to background levels. Hence the influence on the concentrations measured at Mace Head is relatively small, if any. An attempt to quantify this effect from direct measurements of aerosol concentrations at Mace Head, based on differences in concentrations between selected wind directions, showed no clear correlation. Also there was no obvious concentration enhancement when the wind was from the directions of the islands. At low wind speed, the concentrations of super-micron aerosol particles at Mace Head exhibited variability of not more than a factor of 2, and less in elevated wind speeds, although this cannot be directly linked to the offshore plumes. The concentrations of sub-micron aerosol particles are not affected [Kleefeld et al., 2002], in good agreement with other studies of surf aerosols [de Leeuw et al., 2000].”

Surf zone effects at the Mace Head shore are potentially more of a concern but also depend on sampling height. It should be acknowledged that, due to the rugged and modestly-sloping foreshore at Mace Head, the breaking surf is limited to about 10 m stretch in contrast to the much more extensive flat surf stretched used in the Clarke et al. (2006) study. In this section, we will address the questions: is submicron aerosol influenced by the local surf zone at Mace Head and are organic aerosol dominated by coastal contamination?

During the NAMBLEX experiment, Norton et al. (2006), using micrometeorological measurements, demonstrated some increase in surface drag between the 10 m and 15 m sampling levels and attributed this to the top of the developing shore internal layer reaching this height; however, it should be noted that the increase was not very

## Mace Head aerosol

C. O'Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



strong and could also be attributed to increased drag due to the laboratory buildings which extended to 8 m and were located at the foot of the tower. During the same experiment, Coe et al. (2008) evaluated the gradient in particle number concentration and non-refractory aerosol chemical species concentration (e.g. nss-sulphate, OM, ammonium etc.) using an AMS switching between to sampling manifolds sampling from 7 m and 22 m heights on the main Mace Head 22 m sampling tower. While some differences were seen in total number concentration, and attributed to shore-line coastal nucleation events, no discernable difference was found amongst the non-refractory aerosol chemical species suggesting no discernable gradient in the aerosol species measured over these heights. They also report that even particles in the 1 to 3  $\mu\text{m}$  range showed no evidence of the surface layer perturbing the concentration of particles at 7 m above ground level – this is the size range which would be almost exclusively dominated by sea-salt.

The aforementioned study was expanded upon by Ceburnis et al. (2008) who deployed a Mace Head clean-sector gradient aerosol chemical flux experiment with the initial aim of quantifying the source of the water insoluble organic matter (WIOM) aerosol component, previously attributed to sea-spray production by O'Dowd et al. (2004) and studies thereafter. In contrast to the Coe et al. (2008) height-switching gradient evaluation which was conducted over 15 m height difference on short time-scales, Ceburnis et al. (2008) conducted gradient flux experiments over a 32 m gradient and over time-scales of the order of a week. Such an approach can detect very subtle gradients for flux determining purposes which would not be detectable in the gradient-switching approach. At this point it is appropriate to introduce the concepts of the flux footprint and the concentration. The flux footprint is the upwind area which contributes to the measured turbulent flux signal while the concentration footprint is the upwind area which contributes to the concentration signal. Geever et al. (2005) calculated the flux footprint from the Mace Head 22 m tower as starting  $\sim 200$  m upwind (to the west) of the tower, peaking  $\sim 800$ – $900$  m offshore, and extending up to 7–8 km over

the water. In contrast, the concentration footprint ranges from 10–100 times the flux footprint depending on the meteorological conditions.

Ceburnis et al. (2008) demonstrated that sea-salt always possessed a negative gradient with height, pointing to a surface source, while nss-sulphate and water soluble organic matter (WSOM) exhibited a positive gradient with height, pointing to a surface sink within the flux footprint and a source within or above the boundary layer or a source upwind of the flux footprint. While nss-sulphate is exclusively formed through secondary processes, WSOM can either be secondary or processed primary WIOM formed upwind of the footprint. WIOM, on the other hand (Fig. 10), exhibited both positive and negative gradients, indicating both a surface source and a surface sink. These dual results leads to two important conclusions: the first is that WIOM is the clean marine air is indeed associated with POM sea-spray production (rather than longrange transport of pollution) and, secondly, WIOM can be produced upwind of the flux footprint and is not a surfzone or coastal artefact. The Ceburnis et al. (2008) experiment clearly indicates that at least the WIOM component of OM cannot exclusively dismissed as a coastal aretefact. What about WSOM and sea-salt? The gradient profiles demonstrate always a surface source for sea-salt, as to be epected, and never a near-coast surface source for WSOM.

The potential for coastal aretefacts was further explored in a case study by Rinaldi et al. (2009), where a connected flow experiment between an upwind ship and shore-based measurements at Mace Head was reported. The comparison was limited to 3 sampling periods from 12 June to 5 July, with between 36 and 80 h sampling time depending on the sample, with the Research Vessel Celtic Explorer being 200–350 km upwind of Mace Head. The aim of the comparison was not to determine if what was measured off-shore was identical to that at Mace Head since such a scenario would represent an unrealistic steady-state between source, evolution and sink processes over large areas when it is clear there are differences in both meteorology and ocean-surface composition over such areas, but more so, to evaluate if there was a consistently higher mass contribution from particular aerosol chemical species which could

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



## Mace Head aerosol

C. O'Dowd et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

be attributed to coastal production artefacts at Mace Head. The comparison cases revealed comparable, if not even higher, off-shore concentrations for nss-sulphate, WSOM, WIOM, and MSA. Sea-salt, in supermicron sizes exhibited 40 % higher mass at Mace Head with no discernable differences for submicron sea-salt. It has previously been shown that breaking surf preferentially produces supermicron salt particles (de Leeuw et al., 2000), suggesting that part of the difference in supermicron sea-salt mass is due to surf production in the coastal zone; however, some of the enhanced mass observed can be attributed to the wind speed at Mace Head which was 1.8 times higher than the offshore wind encountered by the ship. The above studies suggest that there is no discernable enhancement in submicron sea-salt or primary organic sea-spray as a result of surf zone breaking waves at sampling heights of 7 m or higher. A recent study utilised AMS-derived sea-salt mass concentrations (Ovadnevaite et al., 2012) to develop a submicron sea-salt mass source function for wind speeds up to  $26 \text{ m s}^{-1}$ , at which 10 m – height sea-salt mass concentrations reached a maximum of  $2.5 \mu\text{g m}^{-3}$ . Three well known source functions, that of Martensson et al. (2003), Fuentes et al. (2010) and Gong et al. (2003) were applied to predict the resulting mass concentrations for the observed boundary layer height and two day wind speed evolution – all were found to predict significantly, and unrealistically, higher mass concentrations that resulted in 3–10 times higher concentrations. If Mace Head was subjected to notable coastal submicron surf contamination, one may anticipate the actual mass measurements being substantially greater than the predicted values.

Facchini et al. (2008b) also presented results conclusively confirming that the WIOM component of marine air is associated with primary sea-spray. In doing so, they illustrated that the WIOM/sea-salt ratio fingerprint as a function of size was almost identical for samples collected in air at Mace Head, in air off-shore on the Celtic Explorer, and in bubble-bursting laboratory experiments on board the Celtic Explorer (Fig. 11). The similarity in the ratio/size fingerprint confirms that, at least, the relative proportions of WIOM as a function of size are not influenced by coastal artefacts.

## 4 Discussion and conclusions

Patterns of biological productivity are different from ocean to ocean, and is especially evident when comparing chlorophyll *a* concentration fields in the contrasting South Pacific and North Atlantic Oceans, the former are being more patchy but homogeneously distributed throughout the year, while the latter experiences a high seasonal variability, but with concentrations much more uniform over the area. Moreover, the chlorophyll *a* concentrations over the South Pacific are consistently lower (monthly concentrations varying  $\sim 0.1 \text{ mg m}^{-3}$  with narrow bands peaking at  $\sim 0.4 \text{ mg m}^{-3}$  at the equator) than those seen in the North Atlantic (where monthly average concentrations range from  $\sim 0.2 \text{ mg m}^{-3}$  for low biological activity periods to  $\sim 0.7 \text{ mg m}^{-3}$  for high biological activity periods). Overall, the biomass abundance is far greater in the North Atlantic compared to the equatorial and South Pacific and the higher chlorophyll *a* concentrations encountered by Shank et al. (2012) over the Pacific are at the lower end of the values reported over the N.E. Atlantic by O'Dowd and colleagues. Consequently, it is no surprise that the OM concentrations observed by Shank et al. (2012) are at the lower end of the concentrations observed at Mace Head.

What is striking in the difference between the two datasets is that the relationship between OM and BC for BC mass less than  $15 \text{ ng m}^{-3}$  in Shank et al. (2012) is highly correlated ( $R^2 = 0.66$ ), while neither OM versus BC at concentrations between  $0\text{--}15 \text{ ng m}^{-3}$  and  $15\text{--}50 \text{ ng m}^{-3}$  measured at Mace Head are correlated ( $R^2 = 0.006$  and  $R^2 = 0.046$ , respectively), despite peak OM mass concentrations reaching an order of magnitude higher in the Mace Head/Atlantic. In addition, the OM/BC ratios are at between  $3\text{--}100$  times larger over the Atlantic compared to the Pacific. The parameters most comparable in the Shank et al. (2012) Pacific studies and those at Mace Head are the OM-BC absolute mass concentrations, their inter-correlations, and their relative mass ratios; however, the intercomparison of these parameters point to the conclusion that even OM present at Mace Head (N.E. Atlantic) at concentrations more than an order of magnitude higher than in the Pacific can be regarded as almost exclusively

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



natural biogenic while the OM at similar low levels of BC over the Pacific can be regarded as predominantly anthropogenic.

Reviewing the other evidence available to elucidate the pedigree of the maritime nature of marine aerosol sampled under Mace Head clean air criteria, we can summarise the following:

- Over 25 yr, anthropogenic sulphate aerosol concentrations have reduced to 20–25 % of their initial values so that the anthropogenic contamination of the N.E. Atlantic has greatly reduced to a similar extent;
- Clean-sector sampling based on wind direction alone is subject to significant anthropogenic contamination from recirculating European continental air;
- Sulphate isotope analysis show that the biogenic contribution can be as high as 70–90 % over the central N. Atlantic;
- Carbon isotope analysis show that 80 % of OM measured at Mace Head under clean air criteria is marine biogenic in origin;
- Aerosol mass spectral analysis reveals the clear dominance of a unique marine POM marine aerosol type during organic sea-spray plumes;
- Comparison of aerosol-speciated chemical mass at Mace Head and in connected flow upwind and offshore show no evidence for coastal enhancement of artefacts in submicron sizes;
- Gradient measurements between 7 m and 22 m at Mace Head, using an aerosol mass spectrometer, revealed no discernible difference, and consequently, no coastal, surf zone or tidal effects;
- Gradient flux measurements demonstrate that OM production is not unique to the coastal zone.

Mace Head aerosol

C. O’Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In conclusion, the Mace Head sampling criteria, published most recently by Ceburnis et al. (2011), can be used to ensure anthropogenic and coastal effects are sufficiently minimised so as to result in a dominant, if not at times, an overwhelming, natural marine aerosol signal.

5 *Acknowledgements.* This work was supported by the EPA, HEA, EC (under MAP, EUCAARI, EUSAAR and ACTRIS), SFI and ESA-SSE-OSSA. We thank Aditya Vaishya for the wind speed analysis.

## References

- 10 Bates, T., Quinn, P., Coffman, D., Johnson, J., and Middlebrook, A.: Dominance of organic aerosols in the marine boundary layer over the Gulf of Maine during NEAQS 2002 and their role in aerosol light scattering, *J. Geophys. Res.*, 110, D18202, doi:10.1029/2005JD005797, 2005.
- 15 Cavalli, F., Facchini, M. C., Decesari, S., Mircea, M., Emblico, L., Fuzzi, S., Ceburnis, D., Yoon, Y. J., O'Dowd, C. D., Putaud, J. P., and Dell'Acqua, A.: Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic, *J. Geophys. Res.-Atmos.*, 109, D24215, doi:10.1029/2004jd005137, 2004.
- 20 Ceburnis, D., O'Dowd, C. D., Jennings, S. G., Facchini, M. C., Emblico, L., Decesari, S., Fuzzi, S., and Sakalys, J.: Elucidation of production mechanisms of water soluble and insoluble organic carbon in marine air and associated gradient fluxes over the Northeast Atlantic, *Geophys. Res. Lett.*, 35, L07804, doi:10.1029/2008GL033462, 2008.
- 25 Ceburnis, D., Garbaras, A., Szidat, S., Rinaldi, M., Fahrni, S., Perron, N., Wacker, L., Leinert, S., Remeikis, V., Facchini, M. C., Prevot, A. S. H., Jennings, S. G., Ramonet, M., and O'Dowd, C. D.: Quantification of the carbonaceous matter origin in submicron marine aerosol by  $^{13}\text{C}$  and  $^{14}\text{C}$  isotope analysis, *Atmos. Chem. Phys.*, 11, 8593–8606, doi:10.5194/acp-11-8593-2011, 2011.
- Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, 326, 655–661, 1987.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Mace Head aerosol

C. O'Dowd et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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

5 Coe, H., Allan, J. D., Alfarra, M. R., Bower, K. N., Flynn, M. J., McFiggans, G. B., Topping, D. O., Williams, P. I., O'Dowd, C. D., Dall'Osto, M., Beddows, D. C. S., and Harrison, R. M.: Chemical and physical characteristics of aerosol particles at a remote coastal location, Mace Head, Ireland, during NAMBLEX, *Atmos. Chem. Phys.*, 6, 3289–3301, doi:10.5194/acp-6-3289-2006, 2006.

10 de Leeuw, G., Neele, F. P., Hill, M., Smith, M. H., and Vignati, E.: Sea spray aerosol production by waves breaking in the surf zone, *J. Geophys. Res.*, 105, 29397–29409, 2000.

de Leeuw, G., Andreas, E. L., Anguelova, M. D., Fairall, C. W., Lewis, E. R., O'Dowd, C., Schulz, M., and Schwartz, S. E.: Production Flux of Sea-Spray Aerosol, *Rev. Geophys.*, 49, RG2001, doi:10.1029/2010RG000349, 2011.

15 Dall'Osto, M., Ceburnis, D., Martucci, G., Bialek, J., Dupuy, R., Jennings, S. G., Berresheim, H., Wenger, J., Healy, R., Facchini, M. C., Rinaldi, M., Giulianelli, L., Finessi, E., Worsnop, D., Ehn, M., Mikkilä, J., Kulmala, M., and O'Dowd, C. D.: Aerosol properties associated with air masses arriving into the North East Atlantic during the 2008 Mace Head EUCAARI intensive observing period: an overview, *Atmos. Chem. Phys.*, 10, 8413–8435, doi:10.5194/acp-10-8413-2010, 2010.

20 Geever, M., O'Dowd, C. D., van Ekeren, S., Flanagan, R., Nilsson, D. E., de Leeuw, G., and Rannik, U.: Sub-micron sea-spray fluxes, *Geophys. Res. Lett.*, 32, L15810, doi:10.1029/2005GL023081, 2005.

25 Facchini, M. C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D., and O'Dowd, C. D.: Important Source of Marine Secondary Organic Aerosol from Biogenic Amines, *Environ. Sci. Technol.*, 42, 9116–9121, doi:10.1021/Es8018385, 2008a.

30 Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, *Geophys. Res. Lett.*, 35, L17814, doi:10.1029/2008gl034210, 2008b.

Fuentes, E., Coe, H., Green, D., de Leeuw, G., and McFiggans, G.: On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol –

## Mace Head aerosol

C. O'Dowd et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Part 1: Source fluxes, *Atmos. Chem. Phys.*, 10, 9295–9317, doi:10.5194/acp-10-9295-2010, 2010.

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

Haywood, J. M., Osborne, S. R., Francis, P. N., Keil, A., Formenti, P., Andreae, M. O., and Kaye, P. H.: The mean physical and optical properties of regional haze dominated by biomass burning aerosol measured from the C-130 aircraft during SAFARI 2000, *J. Geophys. Res.*, 108, 8473, doi:10.1029/2002JD002226, 2003.

Jennings, S. G., Kleefeld, C., O'Dowd, C. D., Junker, C., Spain, T. G., O'Brien, P., Roddy, A. F., and O'Connor, T. C.: Mace head atmospheric research station characterization of aerosol radiative parameters, *Boreal Environ. Res.*, 8, 303–314, 2003.

Johnson, D. W., Osborne, S., Wood, R., Suhre, K., Johnson, R., Businger, S., Quinn, P. K., Bates, T., Wiedensohler, A., Durkee, P. A., Russell, L. M., Andreae, M. O., O'Dowd, C., Noone, K. J., Bandy, B., Rudolph, J., and Rapsomanikis, S.: An overview of the Lagrangian experiments undertaken during the North Atlantic Regional Aerosol Characterisation Experiment (ACE – 2), *Tellus*, 52B, 290–320, 2000.

Kleefeld, C., O'Dowd, C. D., O'Reilly, S., Jennings, S. G., Aalto, P., Becker, E., Kunz, G., and de Leeuw, G.: Relative contribution of sub and super micron particles to aerosol light scattering in the marine boundary layer, *J. Geophys. Res.*, 107, D19, doi:10.1029/2000JD000262, 2002.

Kunz, G. J., de Leeuw, G., Becker, E., and O'Dowd, C. D.: Lidar observations of atmospheric boundary layer structure and sea spray aerosol plumes generation and transport at Mace Head, Ireland (PARFORCE experiment), *J. Geophys. Res.*, 107, doi:10.1029/2001JD001240, 2002.

Lapina, K., Heald, C. L., Spracklen, D. V., Arnold, S. R., Allan, J. D., Coe, H., McFiggans, G., Zorn, S. R., Drewnick, F., Bates, T. S., Hawkins, L. N., Russell, L. M., Smirnov, A., O'Dowd, C. D., and Hind, A. J.: Investigating organic aerosol loading in the remote marine environment, *Atmos. Chem. Phys.*, 11, 8847–8860, doi:10.5194/acp-11-8847-2011, 2011.

Lin, C. T., Baker, A. R., Jickells, T. D., Kelly, S., and Lesworth, T.: An assessment of the significance of sulphate sources over the Atlantic Ocean based on sulphur isotope data, *Atmos. Environ.*, 62, 615–621, 2012.

## Mace Head aerosol

C. O'Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Mazzera, D. M., Lowenthal, D. H., Chow, J. C., Watson, J. G., and Grubisic, V.: PM<sub>10</sub> measurements at McMurdo Station, Antarctica, *Atmos. Environ.*, 35, 1891–1902, doi:10.1016/S1352-2310(00)00409-X, 2001.

Martensson, E. M., Nilsson, E. D., de Leeuw, G., Cohen, L. H., and Hansson, H. C.: Laboratory simulations and parameterization of the primary marine aerosol production, *J. Geophys. Res.-Atmos.*, 108, 4297, doi:10.1029/2002jd002263, 2003.

McArdle, N., Liss, P., and Dennis, P.: An isotopic study of atmospheric sulphur at three sites in Wales and at Mace Head, Eire, *J. Geophys. Res.-Atmos.*, 102, 31079–31094, 1998.

Norton, E. G., Vaughan, G., Methven, J., Coe, H., Brooks, B., Gallagher, M., and Longley, I.: Boundary layer structure and decoupling from synoptic scale flow during NAMBLEX, *Atmos. Chem. Phys.*, 6, 433–445, doi:10.5194/acp-6-433-2006, 2006.

Novakov, T., Menon, S., Kirchstetter, T. W., Koch, D., and Hansen, J. E.: Aerosol organic carbon to black carbon ratios: Analysis of published data and implications for climate forcing, *J. Geophys. Res.*, 110, D21205, doi:10.1029/2005JD005977, 2005.

O'Connor, T. C., Jennings, S. G., and O'Dowd, C. D.: Highlights of fifty years of atmospheric aerosol research at Mace Head, *Atmos. Res.*, 90, 338–355, doi:10.1016/j.atmosres.2008.08.014, 2008.

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

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J. P.: Biogenically driven organic contribution to marine aerosol, *Nature*, 431, 676–680, doi:10.1038/Nature02959, 2004.

Ovadnevaite, J., O'Dowd, C., Dall'Osto, M., Ceburnis, D., Worsnop, D. R., and Berresheim, H.: Detecting high contributions of primary organic matter to marine aerosol: A case study, *Geophys. Res. Lett.*, 38, L02807, doi:10.1029/2010gl046083, 2011a.

Ovadnevaite, J., Ceburnis, D., Bialek, J., Monahan, C., Martucci, G., Rinaldi, M., Facchini, M. C., Berresheim, H., Worsnop, D. R., and O'Dowd, C. D.: Primary Marine Organic Aerosol: A Dichotomy of Low Hygroscopicity and High CCN Activity, *Geophys. Res. Lett.*, 38, L21806, doi:10.1029/2011GL048869, 2011b.

Quinn, P. K. and Bates, T. S.: Regional aerosol properties: Comparisons of boundary layer measurements from ACE 1, ACE 2, aerosols99, INDOEX, ACE asia, TARFOX, and NEAQS, *J. Geophys. Res.*, 110, D14202, doi:10.1029/2004JD004755, 2005.

## Mace Head aerosol

C. O'Dowd et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

- Reid, J. S., Koppmann, R., Eck, T. F., and Eleuterio, D. P.: A review of biomass burning emissions part II: intensive physical properties of biomass burning particles, *Atmos. Chem. Phys.*, 5, 799–825, doi:10.5194/acp-5-799-2005, 2005.
- 5 Rinaldi, M., Facchini, M. C., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Ehn, M., Kulmala, M., de Leeuw, G., and O'Dowd, C. D.: On the representativeness of coastal aerosol studies to open ocean studies: Mace Head – a case study, *Atmos. Chem. Phys.*, 9, 9635–9646, doi:10.5194/acp-9-9635-2009, 2009.
- 10 Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Fuzzi, S., Ceburnis, D., O'Dowd, C. D., Sciare, J., Burrows, J. P., Vrekoussis, M., Ervens, B., Tsigaridis, K., and Facchini, M. C.: Evidence of a natural marine source of oxalic acid and a possible link to glyoxal, *J. Geophys. Res.*, 116, D16204, doi:10.1029/2011JD015659, 2011.
- Savoie, D. L., Arimoto, R., Keene, W. C., Prospero, J. M., Duce, R. A., and Galloway, J. N.: Marine biogenic and anthropogenic contributions to non-sea-salt sulfate in the marine boundary layer over the North Atlantic Ocean, *J. Geophys. Res.*, 107, 4356, doi:10.1029/2001JD000970, 2002.
- 15 Sciare, J., Favez, O., Sarda-Esteve, R., Oikonomou, K., Cachier, H., and Kazan, V.: Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source, *J. Geophys. Res.-Atmos.*, 114, D15302, doi:10.1029/2009jd011998, 2009.
- 20 Singh, H. B., Anderson, B. E., Brune, W. H., Cai, C., Cohen, R. C., Crawford, J. H., Cubison, M. J., Czech, E. P., Emmons, L., Fuelberg, H. E., Huey, G., Jacob, D. J., Jimenez, J. L., Kaduwela, A., Kondo, Y., Mao, J., Olson, J. R., Sachse, G. W., Vay, S. A., Weinheimer, A., Wennberg, P. O., and Wisthaler, A.: Pollution influences on atmospheric composition and chemistry at high northern latitudes: Boreal and California forest fire emissions, *Atmos. Environ.*, 44, 4553–4564, 2010.
- 25 Shank, L. M., Howell, S., Clarke, A. D., Freitag, S., Brekhovskikh, V., Kapustin, V., McNaughton, C., Campos, T., and Wood, R.: Organic matter and non-refractory aerosol over the remote Southeast Pacific: oceanic and combustion sources, *Atmos. Chem. Phys.*, 12, 557–576, doi:10.5194/acp-12-557-2012, 2012.
- 30 Slingo, A.: Sensitivity of the Earth's radiation budget to changes in low clouds, *Nature*, 343, 49–51, doi:10.1038/343049a0, 1990.
- Yoon, Y. J., Ceburnis, D., Cavalli, F., Jourdan, O., Putaud, J. P., Facchini, M. C., Decesari, S., Fuzzi, S., Sellegri, K., Jennings, S. G., and O'Dowd, C. D.: Seasonal characteristics of



ACPD

13, 7311–7347, 2013

## Mace Head aerosol

C. O'Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Mace Head aerosol

C. O'Dowd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

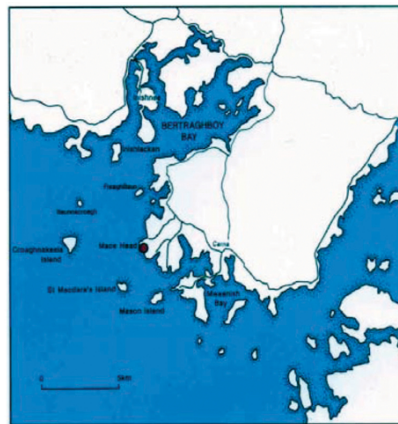
Interactive Discussion

**Table 1.** OM/BC ratios for selected background marine locations and polluted regions.

Location	OM/BC	References
Amsterdam Island (South Indian Ocean) <sup>*3</sup>	60	Sciare et al. (2009)
Point Reyes (North Pacific Ocean) <sup>*2</sup>	15	Sourced from IMPROVE
Mace Head (North Atlantic) <sup>**1</sup>	28	This study
Mace Head (North Atlantic), OM plumes <sup>1</sup>	182	Ovadnevaite et al. (2011)
OOMPH (South Atlantic) <sup>1</sup>	3.2	Sourced from OOMPH
McMurdo (Antarctica) <sup>*3</sup>	2.5	Mazzera et al. (2001)
Southeast Pacific, clean MBL <sup>***1</sup>	10	Shank et al. (2012)
Northeast coast of the US South-westerly flow <sup>1****</sup>	20	Bates et al. (2005)
Northeast coast of the US North-westerly flow <sup>1****</sup>	34	Bates et al. (2005)
Canadian forest fires: fresh/aged <sup>1</sup>	85/25	Singh et al. (2010)
Southwest India <sup>1</sup>	1	Quinn and Bates (2005)
Northeast Asia <sup>1</sup>	8	Quinn and Bates (2005)
Southern Africa <sup>1</sup>	8	Haywood et al. (2003)
Biomass burning	2–17	Reid et al. (2005)
North America <sup>*2,3,4</sup>	2.63–2.91	Novakov et al. (2005)
Europe <sup>*2,3,4</sup>	3.18–3.37	Novakov et al. (2005)
China <sup>*2</sup>	3.29	Novakov et al. (2005)
India <sup>*2,3,4</sup>	2.81	Novakov et al. (2005)
Japan <sup>*2,3,4</sup>	1.81	Novakov et al. (2005)

\* OM/EC calculated from OC/BC with OM/OC = 1.4; \*\* data restricted to BC < 15 ng m<sup>-3</sup>; \*\*\* data restricted to BC < 4.5 ng m<sup>-3</sup>; \*\*\*\* OM/EC;

<sup>1</sup> PM<sub>1</sub>; <sup>2</sup> PM<sub>2.5</sub>; <sup>3</sup> PM<sub>10</sub>; <sup>4</sup> TSP



**Fig. 1.** (Top) Map of Ireland illustrating the location of Mace Head and local area map and (Bottom) Mace Head shore labs and 22 m tower and shore topography at Mace Head.

Mace Head aerosol

C. O’Dowd et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

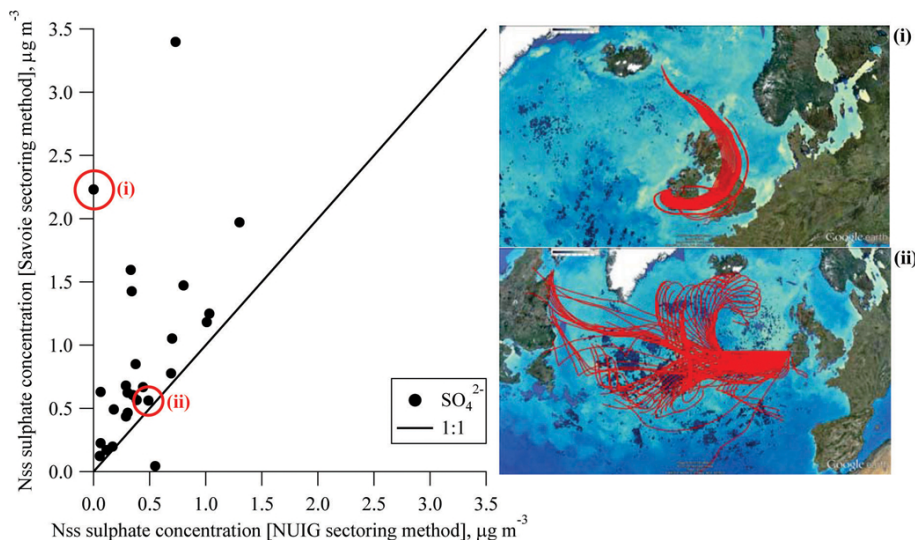
Back Close

Full Screen / Esc

Printer-friendly Version

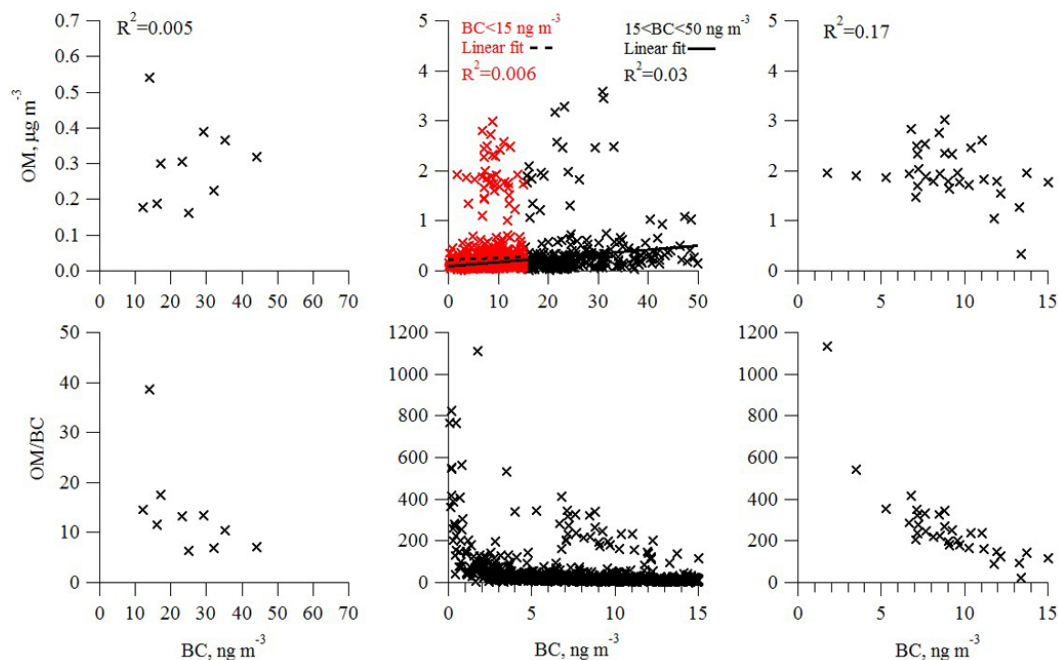
Interactive Discussion



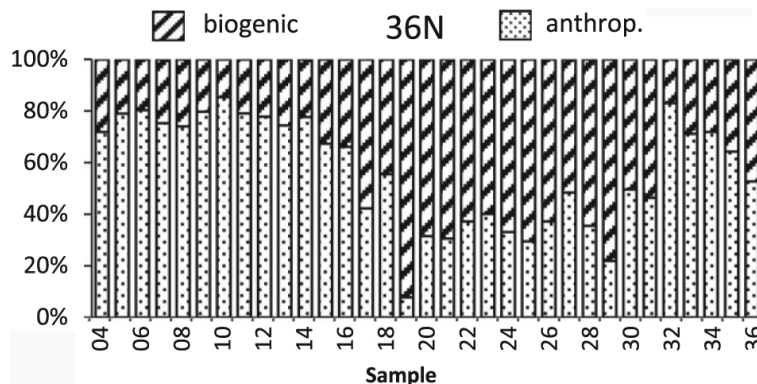


**Fig. 2.** Scatter plot (left) of total nss-sulphate mass concentrations during 2004 at Mace Head obtained by using only the off-shore wind sectoring system (according to Savoie et al., 2002) and the clean marine sectoring system used by NUIG (e.g. Cavalli et al., 2004; Yoon et al., 2007; Ceburnis et al., 2011). Each point corresponds to a one-week sample; however, the total number of hours actual sampling time depends on the clean-sector sampling criteria. On the right, the 96-h air mass back trajectories at 500 m presented in Google Earth<sup>®</sup> represent two contrasting cases often encountered: (i) one week where the Savoie-type sector controller sampled polluted recirculation air based on wind direction while the NUIG system sampled nothing due to the total particle concentration exceeding the nominal threshold concentration of  $700 \text{ cm}^{-3}$  (resulting in the largest difference seen in the scatter plot); and (ii) a week long case where both systems ran coherently as all clean sector trajectories were truly marine (resulting in almost 1 : 1 agreement on the scatterplot).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

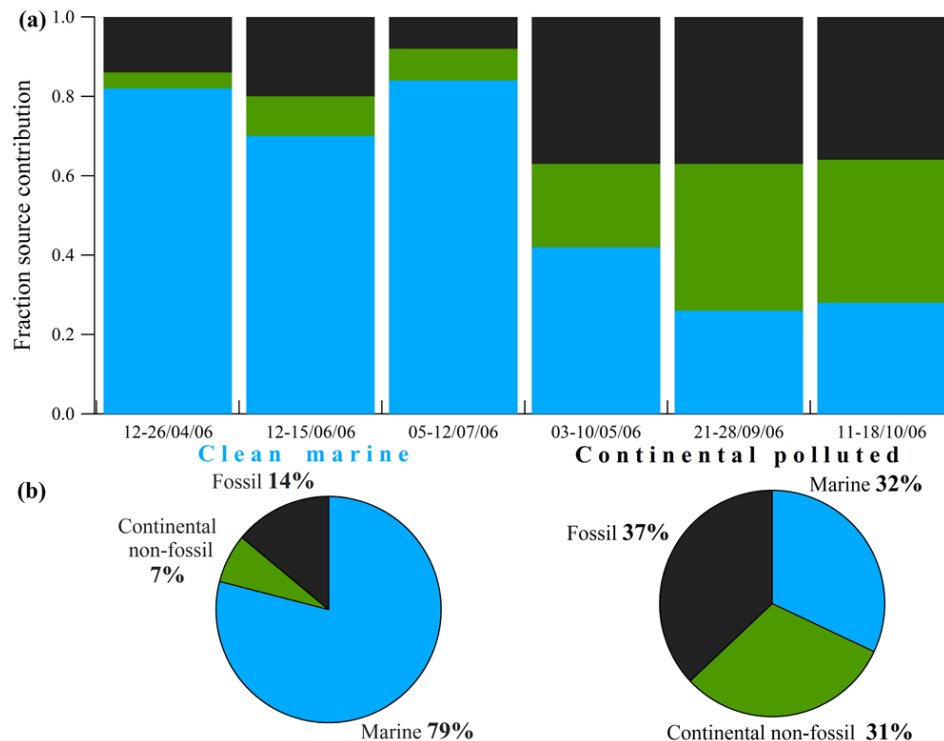



**Fig. 3.** (Top Left) OM versus BC for off-xline sampling ( $\sim 70$  h over 1 week per point) from Yoon et al. (2007). (Bottom Left) Yoon et al. (2007) OM/BC ratios versus BC. (Top Middle) OM vs. BC for three years of online AMS 1-h clean sector Mace Head data, 2009–2011. Data segregated between BC concentrations  $0\text{--}15\text{ ng m}^{-3}$  and  $15\text{--}50\text{ ng m}^{-3}$ . (Bottom Middle) three years OM/BC ratios for  $\text{BC} < 15\text{ ng m}^{-3}$ . (Top Right) OM vs. BC from AMS 1-h average data during primary marine organic plumes (Ovadnevaite et al., 2011). (Bottom Right) OM/EC ratios vs. BC during primary marine organic plumes.



**Fig. 4.** Nss-sulphate contributions from biogenic and anthropogenic sources during a west-east NE Atlantic transect at 36° N, 1 May–15 June 2005. Source apportionment is achieved by sulphur isotope analysis. Figure adapted from Lin et al. (2012), Copyright Elsevier, 2012.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

**Fig. 5. (a)** Source contribution to organic matter in marine and polluted air samples in terms of fossil fuel carbon (black), non-fossil fuel continental carbon (dark green), and marine biogenic carbon (blue) sources; **(b)** same as **(a)** except for average source contributions over all samples for marine and continental air masses. Sourced from Ceburnis et al. (2011) copyright EGU, 2011.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

Navigation: I◀ ▶I

◀ ▶

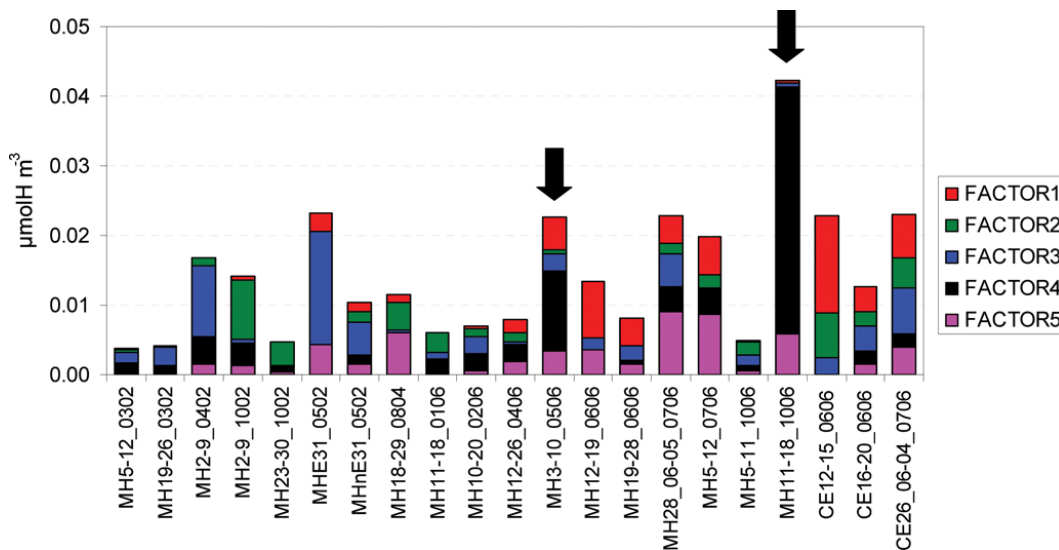
Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

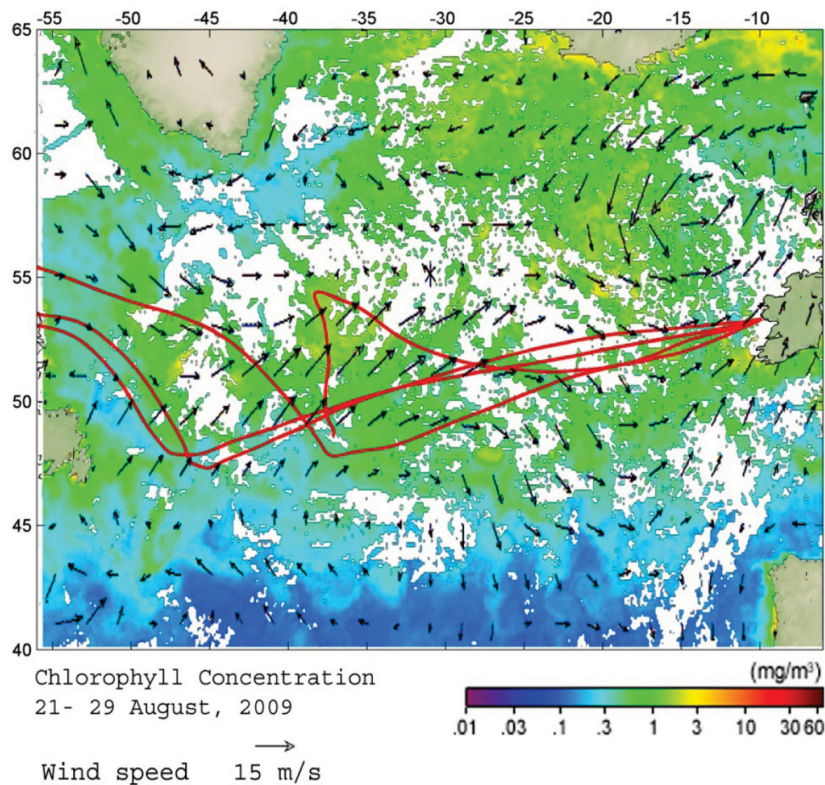




**Fig. 6.** Contribution of the factors identified in marine aerosol WSOC by Decesari et al. (2011). Factor 4 is associated to anthropogenic sources. The black arrows indicate samples collected outside the sector-controlled system, added to the data set for comparison purposes.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)



**Fig. 7.** 96-h, 500 m height air mass back trajectories arriving at Mace Head during the organic plume event ending six-hourly on 16 August 2009. Aqua/MODIS chlorophyll *a* concentration is an average over 21–29 August 2009 and corresponds to the closest coincident retrievable fields due to cloud-contamination. The wind fields are represented as wind vectors (black arrows). Copyright American Geophysical Union, 2011, reprinted from Ovadnevaite et al. (2011a).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

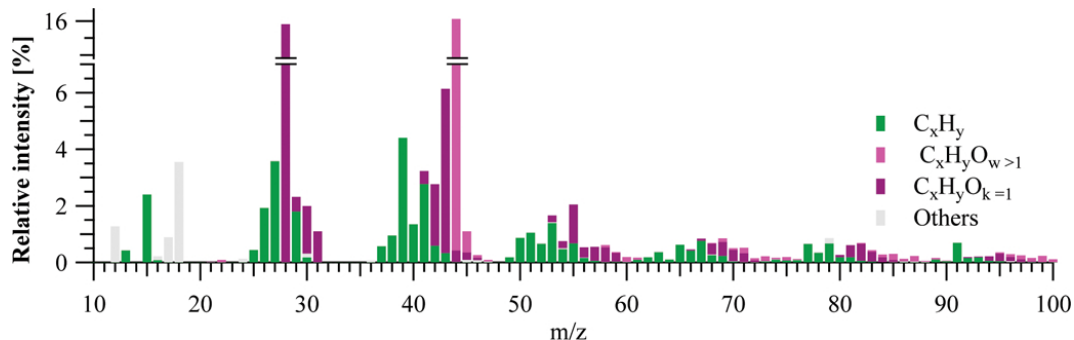
Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



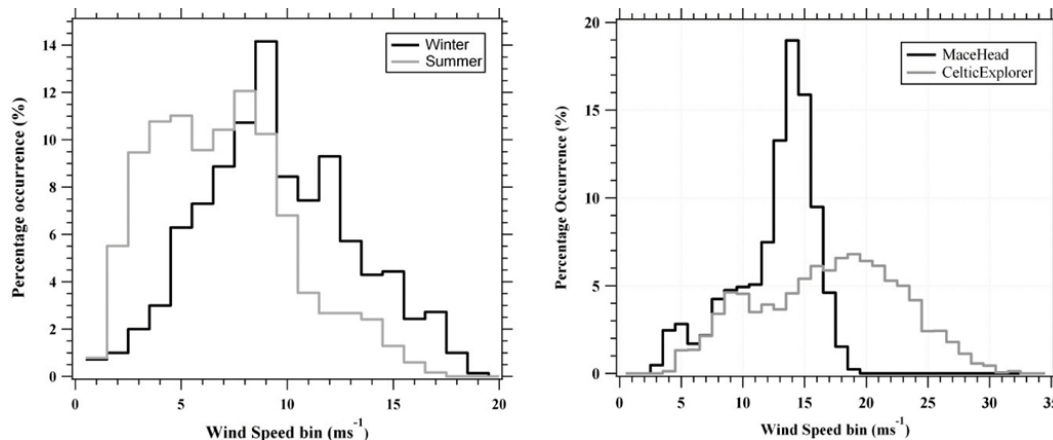


**Fig. 8.** Temporal (UTC) trends of **(a)** wind speed, wind direction, **(b)** CN concentrations and  $PM_{2.5}$  sea-salt mass, **(c)** black carbon mass, AMS-derived  $NO_3$  and  $NH_4$ , and **(d)** AMS-derived total organic, nss-sulphate, CHO and CH mass loadings. Time period in grey colour visually emphasizes the marine primary organic aerosol plume detected (15–16 August). The data gap around 12:00 on the 16th was due to routine AMS calibration. Copyright American Geophysical Union, 2011, reprinted from Ovadnevaite (2011a).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

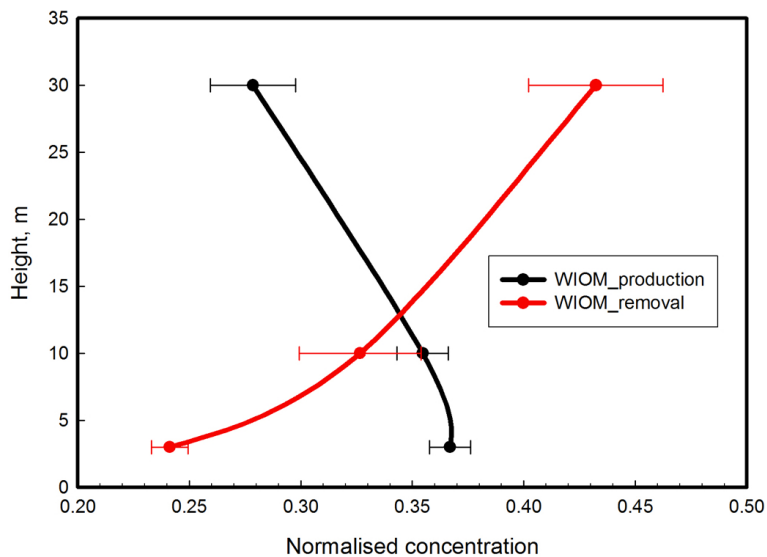

## Mace Head aerosol

C. O'Dowd et al.



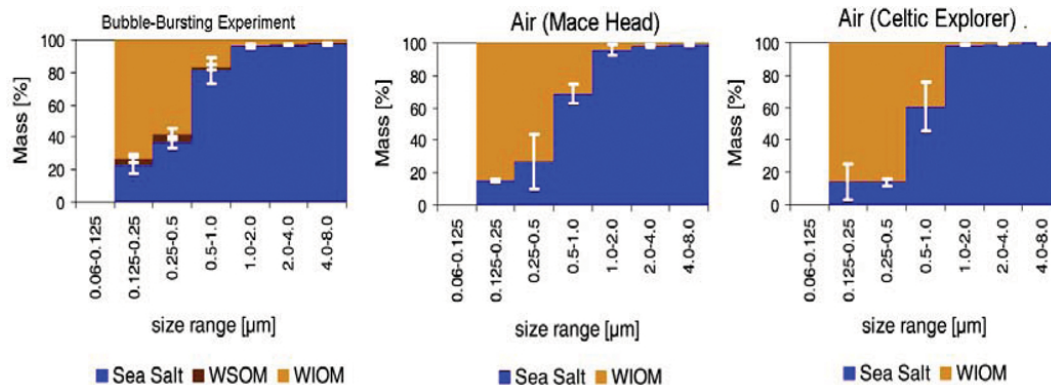
**Fig. 9.** (Left) Percentage frequency occurrence distribution for year 2006 winter and summer seasons. (Right) Data are for hour average over three months for each season. Percentage frequency occurrence distribution for MAP ruise storm off shore from Mace Head compared to wind speed measured at Mace Head: dates: 20–22 June, 2006, Latitude: 55–56.5° N, Longitude: 9.5–11° W.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

**Fig. 10.** Concentration gradients  $PM_{10}$  water insoluble organic matter (WIOM) taken at 3 m, 10 m and 22 m heights. The positive gradient case represents a surface sink while the negative gradient with height represents a surface source.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



**Fig. 11.** WIOM/sea-salt percentage mass contributions as a function of size for laboratory based bubble-bursting experiments on the Celtic Explorer (left), from air samples collected at Mace Head (middle), and from air samples onboard the Celtic Explorer. Copyright American Geophysical Union, 2008, reprinted from Facchini et al. (2008b).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)
