



Do anthropogenic, continental or coastal aerosol sources impact on a marine aerosol signature at Mace Head?

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Abstract. Atmospheric aerosols have been sampled and characterised at the Mace Head north-east (NE) 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 compared to that of aerosol over the pristine open-ocean. Two recurring criticisms relate to the lack of representativeness due to potentially enhanced coastal sources, possibly leading to artificially high values of aerosol concentrations, and to the influence of long-range transport of anthropogenic or continental aerosol and its potential dominance over, or perturbation of, a natural marine aerosol signal. Here, we review the results of previous experimental studies on marine aerosols over the NE Atlantic and at Mace Head with the aim of evaluating their representativeness relative to that of a pristine open-ocean aerosol, i.e. with negligible anthropogenic/continental influence. Particular focus is given to submicron organic matter (OM) aerosol. In summary, no correlation was found between OM and black carbon (BC) in marine air conforming to clean-air sampling criteria, either at BC levels of 0–15 or 15–50 ng m⁻³, suggesting that OM concentrations, up to observed peak values of 3.8 µg m⁻³, are predominantly natural in origin. Sophisticated carbon isotope analysis and aerosol mass spectral finger printing techniques corroborate the conclusion that there is a predominant 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 OM mass concentrations > 3 µg m⁻³ are observed. Similarly, a maximum con-

tribution of 20 % OM mass coming from non-marine sources was established by dual carbon isotope analysis. Further, analysis of a series of experiments conducted at Mace Head conclude that negligible coastal, surf zone, or tidal effects are discernible in the secondary or primary aerosol mass residing in the submicron size range for sampling heights of 7 m and above. The Mace Head marine-air criteria ensure anthropogenic and coastal effects are sufficiently minimised so as to guarantee a predominant, and sometimes overwhelming, natural marine aerosol contribution to the total aerosol population when the criteria are adhered to.

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 overlay 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 from biological processes at the ocean surface (O'Dowd et al., 2004; Facchini et al., 2008b). O'Dowd et al. (2004) identified WIOM

(water-insoluble organic matter) with characteristics unique to surface ocean biological processes, while Facchini et al. (2008a) sampled only POM in the absence of secondary aerosol under controlled bubble-tank laboratory experiments using sea water sampled amidst a strong NE Atlantic bloom. One study by Keene et al. (2007), however, found high WSOM (water-soluble organic matter) enrichment produced in a lab by bubble bursting using oligotrophic water and may be considered as contrasting, in particular, with the Facchini et al. (2008b) study. These two studies are not necessarily comparable: Keene et al. (2007) report high WSOM for low biologically active waters while Facchini et al. (2008a) report high WIOM for highly biologically active waters. The WIOM trend is consistent with an enriched POM source from biological processes; however, there is some suspicion concerning the experimental setup used to quantify the WSOM enrichment in Keene et al. (2007). For example, doubt has been raised regarding the representativeness of real ocean conditions using their sintered glass generator and excessively long bubble rise path which is thought to lead to artificially high enrichment in comparison to other techniques (Fuentes et al., 2010a; King et al., 2012); this would explain the high enrichment of WSOM, particularly in the absence of WIOM, in low biologically active water not seen in Atlantic waters. 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) sulfate produced from the oxidation of dimethyl sulfide (DMS); a hybrid organo-sulfur 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 sulfate dominates over secondary organic aerosol (SOA) as reported in Dall'Osto et al. (2010); however, this study related to a brief snapshot relatively early in the season (late May–early June) when considering that peak productivity and peak OM enrichment occurs in August (noting that in Dall'Osto et al., only concentration and not enrichment was reported).

In pristine environments (e.g. Antarctica, with negligible anthropogenic/continental influence), it can be quite a challenge to characterise the marine aerosol since the primary aerosol depends on dynamics producing the spray, on biological activity which determines the organic matter enrichment, and on oxidant availability which can chemically transform/age POM to SOA-like OM (organic matter) in the spray itself – all processes which are highly variable in time and space (Rinaldi et al., 2010; Decesari et al., 2011). 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, sulfate, and

nitrate 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 data sets. 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 the apparent open-ocean marine aerosol is.

The problem is that, wherever sampling of marine aerosol is conducted, particularly if the focus is on the submicron fraction, there exist 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 NE 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 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

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 marine sector from 190° W through to 290° W (see Fig. 1). Meteorological records show that on average, over 60 % of the air masses arrive at the station in the marine sector (Jennings et al., 2003; O'Connor et al., 2008). Air is sampled

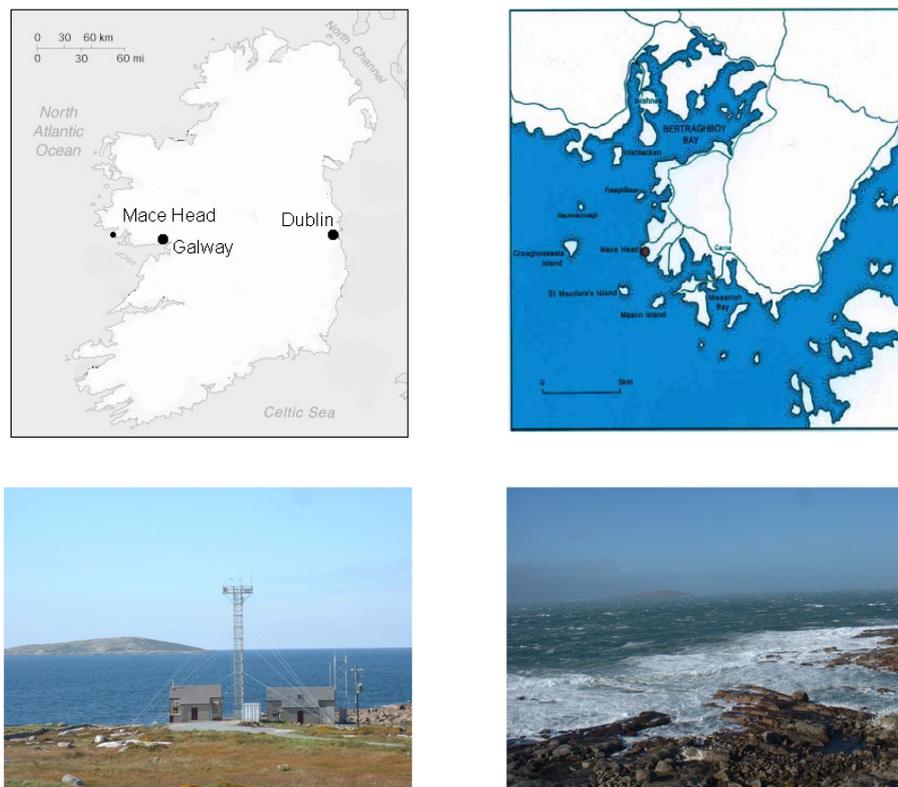


Figure 1. Top: map of Ireland illustrating the location of Mace Head and local area map; bottom: Mace Head shore labs and 22 m tower and shore topography at Mace Head.

from a 10 m high tower and a 22 m tower, both situated ~ 100 m from the shoreline and ~ 50 m from high water (<http://www.macehead.org/>). The shoreline is relatively inhomogeneous and rocky with a slope of $\sim 4^\circ$. 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 surf zone field under moderately windy conditions. Table 1 summarises the various sampling details of the relevant research papers reporting data at Mace Head.

3 Interpretation of previous results

3.1 Aerosol characterisation under wind-sector controlled sampling

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

Some of the first chemical mass measurements undertaken at Mace Head were from August 1989 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-sulfate 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 as, on average, 85–90 % of the nss sulfate in marine flow at Mace Head originating from anthropogenic sources? On face value, this could indeed be the conclusion one arrives at; however, closer examination of the experimental and sampling criteria reveals a different conclusion.

Table 1. Summary of the sampling details from the relevant research papers reporting data at Mace Head.

| Research paper | Sampling details | Observation period |
|---|---|---|
| Savoie et al. (2002) | Onshore winds (undefined sector), 22 m tower | 1989–1990 |
| McArdle et al. (1998) | Non-sectored | 1993–1994 |
| O'Dowd et al. (2004) Cavalli et al. (2004) | Sector 190–300°, CN < 900# cc ⁻¹ , EBC < 70 ng m ⁻³ , 3 m height | 2002 Only six samples collected |
| Geever et al. (2005) | 22 m tower | May–June 2002 |
| Coe et al. (2006) | 7 and 22 m, alternating | July–August 2002 |
| Yoon et al. (2007) Facchini et al. (2008a, b) Rinaldi et al. (2009, 2011) Ceburnis et al. (2011) | Sector 190–300°, CN < 700# cc ⁻¹ , EBC < 50 ng m ⁻³ , 10 m height RV <i>Celtic Explorer</i> 14 m deck | 2002–2004 2006 2006 and 2006–2009 2006 |
| Ceburnis et al. (2008) | 3, 10, 30 m height parallel sampling, sector 190–300°, CN < 700# cc ⁻¹ , EBC < 50 ng m ⁻³ . | 2005 |
| Dall'Osto et al. (2010) Ovadnevaite et al. (2011a, b, 2012) | 10 m height community sampling duct (applies to CN above) | 2008 2009–2010 |

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 marine 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 not only wind direction but also total particle concentration, or condensation nuclei (CN), as the primary controllers for sampling onshore clean marine air masses. Total particle concentration was measured by a TSI 7610 CN particle counter ($D_{50} > 14$ nm), and the counter was set to trigger sampling shutdown if particle counts exceeded 700 particles cm⁻³ (from 2006 onwards, the TSI 7610 model was replaced by the TSI 3010 condensation particle counter ($D_{50} > 10$ nm), effectively reducing the particle number threshold). The sampling shutdown time was set to 30 s, followed by a re-start time of 5 min, resulting in the possibility that the sample could be polluted 10 % of the time; however, this possible pollution sampling time corresponds to the an extreme scenario of the sample switching on and off every 5 min for the duration of the week's sampling, which, of course, does not happen in practice. Conditions suitable for sampling are normally sustained for many hours at a time, and even if they could only be sustained for an hour at a time, this leads to a 1 % contamination time frame. 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 h prior to arrival at Mace Head and EBC (equivalent BC) concentration measured by an Aethalometer (AE-16, Magee Scientific, single wavelength at 880 nm) not exceeding 50 ng m⁻³ as an upper limit. The air mass back trajectories are only used as supporting evidence to show that air of marine origin has spent the last 48 h in the marine boundary layer, as presented by, e.g., Cavalli et al. (2004) and Ceburnis et al. (2011), facilitating wet deposition of pre-existing aerosol particles (e.g. of North American origin) and replenishment with nascent sea-spray aerosol particles. The EBC value of 50 ng m⁻³ is the limit value and should not be confused with the actual values. In practise the actual values in sectored marine air masses are typically 10–20 ng m⁻³ (Cooke et al., 1997; Junker et al., 2006). The mass attenuation coefficient of Aethalometer AE-16 was 16.8 m² g⁻¹. Junker et al. (2006) indicated that thermo-optical method suggested a much higher value (35 m² g⁻¹) in clean marine sector samples, which would result in an even lower threshold BC value of 24 ng m⁻³ and the typical clean marine sector values of only 5–10 ng m⁻³, which would then be comparable to BC values from the pristine environments (Hansen et al., 1988; Hara et al., 2008; Sciare et al., 2009; Shank et al., 2012). In summary it suggests that EBC values reported for MH (Mace Head) are most likely systematically biased high. The choice of CN or particle number concentration and BC mass concentration thresholds is somewhat arbitrary; however, the choice of 700 CN m⁻³ is consistent with studies in the remote Southern Hemisphere; for example, O'Dowd et al. (1997) found

that total CN in pristine air below 53° S over the South Atlantic and Weddell Sea, Antarctica, while generally less than 500 cm⁻³, often reached 700 cm⁻³ in clean air outside new particle production events. Further, Dall'Osto et al. (2010) found that the marine sector CN frequency distribution was bimodal, with a background mode concentration of 400–600 cm⁻³. For EBC, O'Dowd et al. (1993) found that NE Atlantic background marine air masses comprised EBC mass concentrations between 10 and 35 ng m⁻³ while the lowest EBC mass concentration in modified marine air was observed to be 220 ng m⁻³. Cooke et al. (1997) provided statistical evidence that marine air masses with CN concentrations lower than 700 cm⁻³ were associated with EBC concentrations lower than 75 ng m⁻³. Based on these studies, it seemed reasonable to select the stricter threshold of 50 ng m⁻³. The threshold seems to be justified when the correlation between CN number and EBC mass concentration is analysed. The minimum averaging time of an aethalometer, and thus resolution, was 5 min and was further averaged for 1 h which was significantly less noisy than 5 min data: standard deviations for 1 h and 5 min data were 5 ng m⁻³ and 20 ng m⁻³, respectively. For a typical OM plume event, shown in Fig. 2, lasting about 1 day, EBC mass concentration ranged from 4 to 27 ng m⁻³, while CN remained less than 700 cm⁻³ with no correlation being evident ($R^2 = 0.05$). Extending the averaging timescale from 5 to 60 min reduced the standard deviation from 20 to 5 ng m⁻³, thus demonstrating that almost all data reported are indeed above the noise level. For an extended period from 1 January to 31 May 2009, comprising of 995 h of data that meet the criteria of CN less than 700 cm⁻³, wind direction of 190–300°, and non-recirculating marine-sector air mass back trajectories, no correlation is observed either ($R^2 = 0.06$). Regarding the extended case, 1.6 % of the data records reside outside the 50 ng m⁻³ threshold; however, the contaminated samples amount to a negligible percentage of data in this category; in any event, they are removed because they exceed the 50 ng m⁻³ threshold. The lack of correlation between CN and EBC below the 50 ng m⁻³ threshold suggests a credible set of criteria for marine background air mass sampling. The absence of correlation between CN and EBC may be partially attributed to different sources as nucleation events contribute to CN but not EBC. However, any nucleation events would typically exceed the threshold of 700 cm⁻³ by at least 3 times or more and thus be excluded from the regression. Consequently, some of the clean air can, indeed, be excluded, but the conservative approach is useful in avoiding significant contamination of samples by anthropogenic air masses (noting that in polluted air masses, a correlation between CN and EBC would be expected as the peak in both their number (for CN) and mass (for EBC) size distribution occurs over the same size range (30–70 nm)). In any event, exclusion of some clean air certainly does not compromise the integrity of the data and, more importantly, the clean-air data are examined by numerous state-of-the-art

methods discussed below, thereby corroborating the robustness of the clean-sector sampling system.

As it happened, in 2004, both the Savoie-type and the NUIG (National University of Ireland, Galway)-type marine sector controllers were run in parallel and a scatter plot of their relationship is illustrated in Fig. 3 where each point represents nss-sulfate 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 (TSP) matter and the NUIG system used a Berner impactor with an upper size cut of 16 μm 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-sulfate masses compared to the NUIG system, often by a factor of 2 or 3. Also shown in Fig. 3 are two contrasting cases from the 2004 data set, visualised by 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 one in which both systems successfully sampled clean air coherently throughout the week (i.e. due to the lack of circulating air in this case). In summary, Fig. 3 presents compelling evidence that the new sector system is far superior to the system used by Savoie et al. (2002) in ensuring the sampled air is cleaner than ever before. However, the results of this comparison should be considered together with other lines of evidence (carbon isotopes, HR-ToF-AMS (high-resolution time-of-flight aerosol mass spectrometry), HNMR (nuclear magnetic resonance)), all of which are discussed later.

The measurements taken by Savoie et al. (2002) were conducted 25 years 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 refute 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-year old Savoie et al. (2002) study. First, the measurements of nss sulfate by Savoie et al. (2002) related to bulk mass measurements where the nss-sulfate mass is derived from Na and sea-salt sulfate concentrations, both very large numbers, relatively speaking, which result in large errors associated with the derivation of the much smaller nss-sulfate mass. This analytical uncertainty is particularly severe for bulk filter analysis compared to size-segregated impactor sample analysis. Second, the emissions of anthropogenic SO₂ have reduced over the recent 2 decades and the annual average reduction in nss-sulfate mass at Mace Head has reduced by 70 % over the last 10 years (O'Dowd et al., 2013). While sulfate mass trends are not available at Mace Head for the 1990s, SO₂ trends from the nearby Valentia GAW (Global Atmospheric Watch) station (<http://www.emep.int>) reveal an even greater reduction for the previous

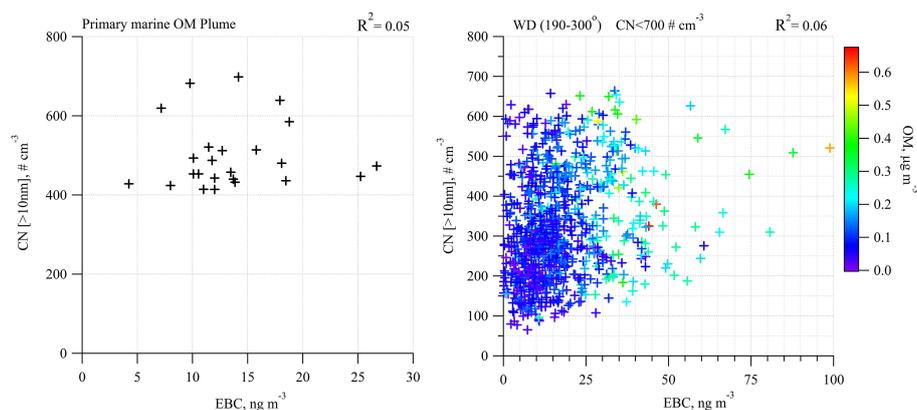


Figure 2. Left: scatter plot of CN vs. EBC for an organic sea-spray event lasting approximately 30 h. Right: scatter plot of CN vs. EBC for 5-month extended (1 January to 31 May 2009) period of combined wind direction (190–300°) and CN (< 700 cm⁻³) concentration sector control.

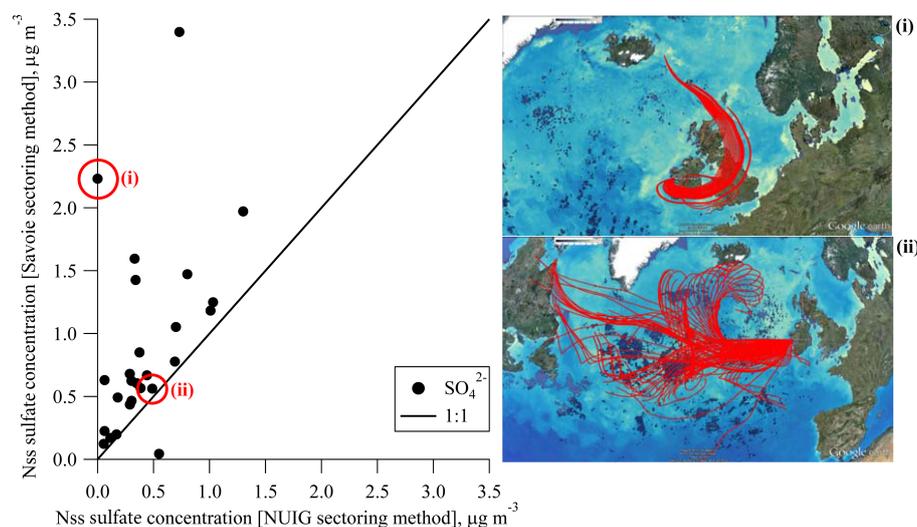


Figure 3. Scatter plot (left) of total nss-sulfate mass concentrations during 2004 at Mace Head obtained by using only the offshore wind sectoring system (according to Savoie et al., 2002) and the clean marine sectoring system used by NUIG (e.g. Cavalli et al., 2004; Yoon et al., 2007; Ceburnis et al., 2011). Each point corresponds to a 1-week sample; however, the total number of hours of 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[®] represent two contrasting cases often encountered: (i) 1 week in which 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 cm⁻³ (resulting in the largest difference seen in the scatter plot); and (ii) a week-long case in which both systems ran coherently as all marine sector trajectories were truly marine (resulting in almost 1 : 1 agreement on the scatter plot).

decade, suggesting that sulfate mass is likely to have reduced by ~ 80 % over the last 25 years. The significant reduction in anthropogenic sulfur 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, an experimental set-up not completely appropriate for the task, high uncertainties associated with the analytical techniques, and the estimated ~ 80 % reduction in anthropogenic sulfate mass since the Savoie et al. (2002) study means that it is simply not justified to claim, these days, that

marine air masses arriving at Mace Head are 85–90 % influenced by anthropogenic aerosols.

3.2 Organic-mass–black-carbon relationships and ratios

In our discussion, we focus mainly on the magnitudes of OM and the OM/EBC ratio to determine the origin of the OM since nss sulfate can have both a natural marine and anthropogenic origin; these results are compared to those of Shank et al. (2012). It should be noted, however, that

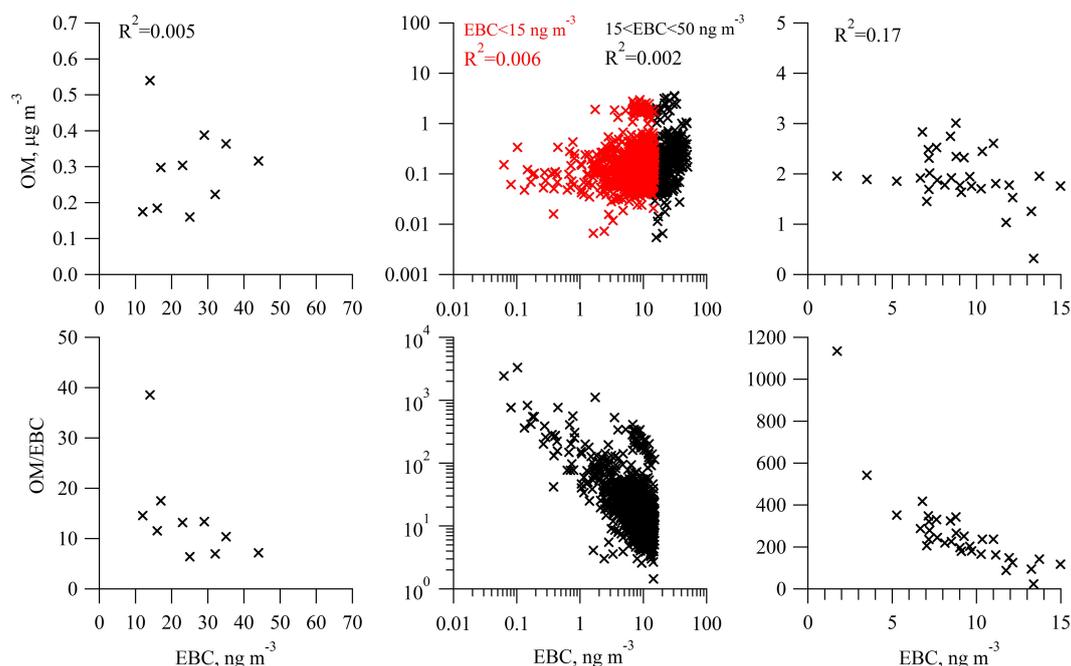


Figure 4. Top left: PM_{10} OM vs. EBC for off-line sampling (per point, ~ 70 h of accumulated marine sector sampling over 1-week period per point) from Yoon et al. (2007). Bottom left: Yoon et al. (2007) OM/EBC ratios vs. EBC. Top middle: OM vs. EBC for 3 years of online AMS 1 h marine sector Mace Head data, 2009–2011. Data segregated between EBC concentrations of $0\text{--}15\text{ ng m}^{-3}$ and $15\text{--}50\text{ ng m}^{-3}$. Bottom middle: 3 years OM/EBC ratios for $\text{EBC} < 15\text{ ng m}^{-3}$. Top right: OM vs. EBC from AMS 1 h average data during primary marine organic plumes (Ovadnevaite et al., 2011b). Bottom right: OM/EBC ratios vs. EBC during primary marine organic plumes.

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) in that Shank et al. (2012) cite this 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 sizes. Consequently, the Shank et al. (2012) OM data refer mostly to only the submicron component.

During the Shank et al. (2012) TAO (Tropical Atmosphere Ocean) cruise (Pacific Ocean $125\text{--}145^\circ\text{ W}$ and $8^\circ\text{ N--}8^\circ\text{ S}$), an OM mass concentration ranging from 0.07 to $0.17\text{ }\mu\text{g m}^{-3}$ was found for screened clean marine air, and a VOCALS (VAMOS Ocean–Cloud–Land Study, in the south-east Pacific region of $15\text{--}30^\circ\text{ S}$) average of $0.07\text{ }\mu\text{g m}^{-3}$ was encountered over Pacific waters. Clean-air conditions were defined as $\text{BC} < 4.5\text{ ng m}^{-3}$ and $\text{CO} < 61\text{ ppb}$. This is compared (Fig. 4) to Mace Head off-line Berner-derived OM mass, ranging from 0.16 to $0.54\text{ }\mu\text{g m}^{-3}$ and $0.05\text{--}3\text{ }\mu\text{g m}^{-3}$ for 3 years of Mace Head on-line AMS data, increasing to $> 3\text{ }\mu\text{g m}^{-3}$ in specific primary organic sea-spray plumes. Shank et al. (2012) concluded that OM was correlated to BC down to concentrations as low as 2 ng m^{-3} and that most of the average OM observed in their Pacific studies was anthro-

pogenic. Further, they also note that it may not be appropriate to fix a threshold OM mass concentration below which the OM can be considered as non-perturbed marine air and suggest that a large fraction of OM mass observed at Mace Head is therefore anthropogenic. There is no justification to conclude that, because high OM is observed over a different ocean, the OM is non-marine. Figure 4 shows the scatter plots of OM vs. EBC for BC mass concentration less than 15 ng m^{-3} for NE 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 $> 3\text{ }\mu\text{g m}^{-3}$, suggesting that the OM reported as marine OM at Mace Head is indeed dominated by clean marine OM aerosol.

Shank et al. (2012) also analysed the OM/BC ratio; they 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/EBC ratios (Table 2) to include additional southern hemisphere oceanic ratios along with our average Mace Head ratios. We find an OM/EBC 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/EBC ratios over EBC mass

concentrations from 0 to 15 ng m^{-3} provide compelling arguments supporting the case that OM observed under the clean-air criteria at Mace Head is indeed dominated by natural marine OM.

In summary, it appears that the OM/EBC ratio is a rather ambiguous parameter to infer the origin of OM, especially when multiple air masses are mixed in the same sample, with the possible exception of when the ratio is extremely low (e.g. 2–5).

3.3 Chemical source apportionment

The first attempt to source apportion the secondary aerosol measured at Mace Head centred on sulfur isotope analysis conducted from 1993 to 1994 by McArdle et al. (1998). The study revealed a maximum biogenic sulfur contribution to total sulfur mass of 30% in spring and summer and significantly less throughout the remainder of the year. In this 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 sulfate aerosol over the Atlantic was undertaken by Lin et al. (2012), when 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 sulfate demonstrates that, close to the US east coast (e.g. sample 4 in Fig. 5, corresponding to -68.9° E , 36.22° N), nss sulfate is 70–80% anthropogenic in origin, while as measurements extended out into the mid-NE Atlantic (sample 19 in Fig. 5, corresponding to -46.27° E , 36.26° N), the natural contribution of sulfate peaked at >90%, although, more generally in this region, it was nearer to 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 is prone to both continental outflow from the US (over the north-west Atlantic) and Europe (over the NE 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 north of Canada, while along the 36° N line, air masses enter the North Atlantic more from the polluted east coast of the US. Similarly, European continental outflow of pollution is more prevalent around southern Portugal, due to persistent high-pressure systems, compared to Mace Head which is more subject to eastwardly tracking cyclones. It was for precisely this reason of regular continental outflow that the ACE-2 (Aerosol Characterization Experiment) Lagrangian experiments started in this region (Johnson et al., 2000).

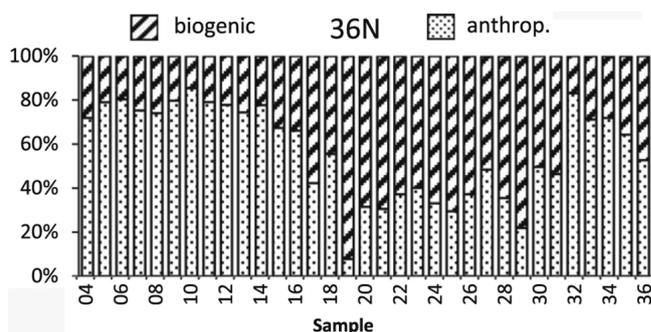


Figure 5. Nss-sulfate contributions from biogenic and anthropogenic sources during a west–east NE Atlantic transect at 36° N , 1 May–15 June 2005. Sample 04 starts at 68.9° W and sample 36 ends at 8.3° W . Source apportionment is achieved by sulfur isotope analysis. Figure adapted from Lin et al. (2012); copyright Elsevier (2012).

Ceburnis et al. (2011) also used isotope analysis to source apportion aerosol at Mace Head; however, their focus was on carbonaceous aerosols, using ^{13}C and ^{14}C isotopes simultaneously to quantify anthropogenic, marine biogenic, and terrestrial non-fossil carbon sources in submicron particles over the NE Atlantic. The contribution of marine biogenic carbon in marine air masses sampled by a sector-controlled system was, on average, $\sim 80\%$, declining to 32% in non-marine air (see Fig. 6). In the marine samples, the remaining sources were 14% fossil fuel and 7% non-fossil fuel. The uncertainty in a single isotope method, e.g. apportioning sources using only ^{13}C , can be dramatically reduced using two isotopes simultaneously and an error minimisation approach as detailed by Ceburnis et al. (2011), thereby constraining not only the fractional contribution of sources, but also the corresponding isotope values of the sources themselves. The error minimisation approach leaves little degrees of freedom for the source isotope values and the fractional contribution of sources, resulting in the final uncertainty in the source isotope values of only $\pm 1\%$ and the uncertainty in the fractional contribution of $\pm 5\%$ (Ceburnis et al., 2011). An entrained FT (free troposphere) aerosol with a significant amount of non-marine OM (continental non-fossil or fossil fuel origin) would have inevitably been identified. The dual isotope approach reveals that only up to a maximum of 20% of such non-marine OM contributes to the total OM mass observed at Mace Head. Ceburnis et al. (2011) reported dual carbon isotope analysis of the total carbon, and, therefore, BC mass, however small, was part of the 21% of non-marine carbon (OC + BC). The variability of BC, or more precisely EBC, has been studied at high resolution with typical concentrations of $10\text{--}20 \text{ ng m}^{-3}$ in sectorised marine air masses occasionally reaching, but never exceeding, 50 ng m^{-3} . It must be stressed that EBC can significantly overestimate BC concentration by up to 50% or more due to the reasons discussed above. There was, indeed, an OM component that

Table 2. OM/EBC ratios for selected background marine locations and polluted regions. IMPROVE: Interagency Monitoring of Protected Visual Environments; OOMPH: Organics Over the ocean Modifying Particles in both Hemispheres; MBL: marine boundary layer.

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

^a OM/BC calculated from OC/BC with OM/OC = 1.4. (OC = organic carbon.)

^b data restricted to EBC < 15 ng m⁻³.

^c data restricted to BC < 4.5 ng m⁻³.

^d OM/EC.

¹ PM₁; ² PM_{2.5}; ³ PM₁₀; ⁴ TSP.

accompanied BC concentration, but there were only three samples for which the anthropogenic fraction of OM was unambiguously determined by isotope analysis. Ceburnis et al. (2011) reported (Table 2 of Ceburnis et al., 2011) that anthropogenic OM varied in the range of 13–24 % or 24–79 ng m⁻³ in clean marine air masses, and the variability could not be linked to specific air masses (Fig. 1 of Ceburnis et al., 2011).

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 (¹H 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 the spectral profile of which 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 marine sector; it was added to the data set for comparison purposes (Fig. 7) and was attributed to an-

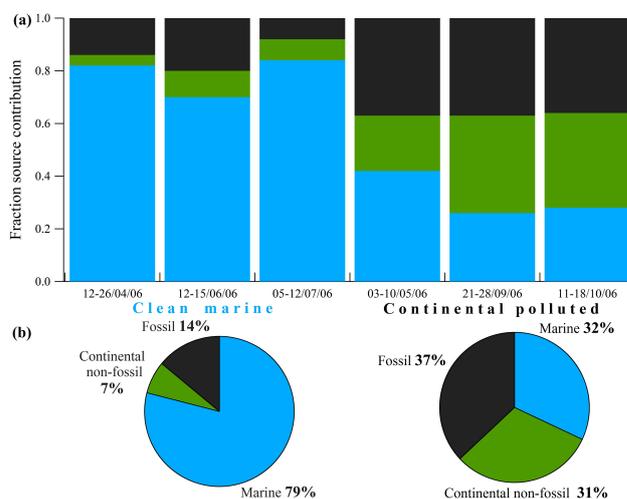


Figure 6. (a) Source contribution to organic matter in marine and polluted air samples in terms of fossil fuel carbon (black), non-fossil fuel continental carbon (dark green), and marine biogenic carbon (blue) sources; (b) same as (a) except for average source contributions over all samples for marine and continental air masses. Sourced from Ceburnis et al. (2011); copyright EGU (2011).

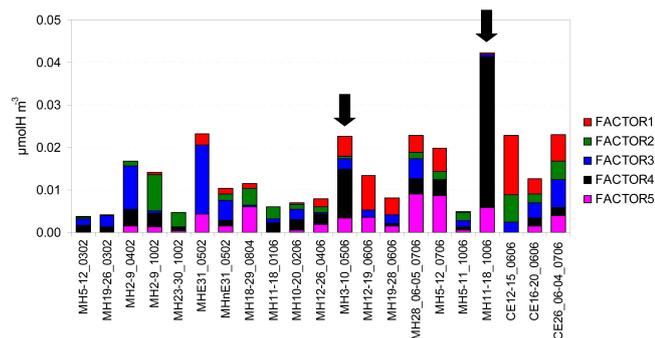


Figure 7. Contribution of the factors ($\mu\text{M m}^{-3}$) identified in marine aerosol WSOC by Decesari et al. (2011). Factor 4 is associated with anthropogenic sources. The black arrows indicate samples collected outside the sector-controlled system, added to the data set for comparison purposes. Each bar represents one sample from Mace Head (MH) or the *Celtic Explorer*. MH5-12_0302 means Mace Head sample from 5 to 12 March 2002.

thropogenic 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 data set investigated by Decesari et al. (2011) is 17% ($\pm 13\%$), in 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 advent of on-line aerosol mass spectrometry, real-time 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. 8 illustrates that the air mass back trajectories advected over chlorophyll *a* rich and stormy waters upwind, while Fig. 9 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 ob-

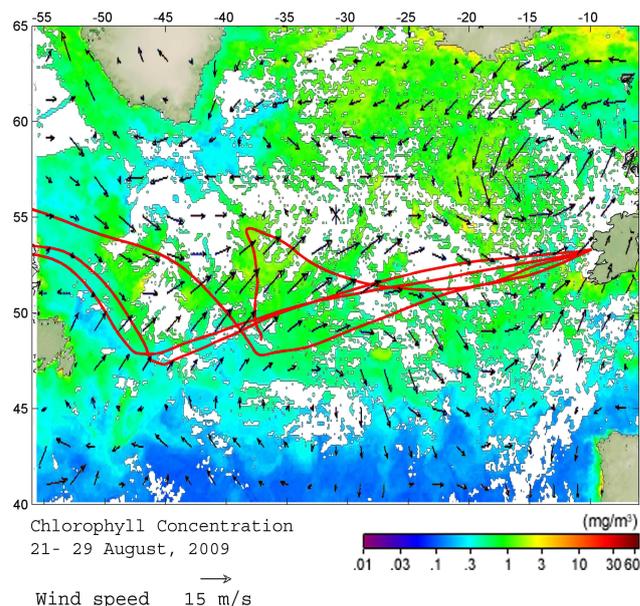


Figure 8. 96 h, 500 m height air mass back trajectories arriving at Mace Head during the organic plume event ending at 00:00, 06:00, 12:00 and 18:00 UTC on the 16 August 2009. Aqua/MODIS chlorophyll *a* concentration is given as an average for 21–29 August 2009 and corresponds to the closest coincident 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).

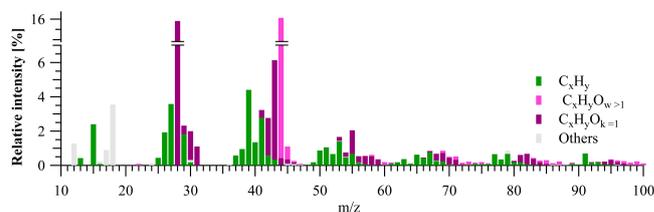


Figure 9. HR-ToF-AMS mass spectra (major organic family CH and CHO, only) of marine organic plume detected on the 15–16 August 2009 at Mace head, Ireland. Copyright American Geophysical Union (2011); reprinted from Ovadnevaite et al. (2011a).

served OM/EBC 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, 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 surf zone artefacts along with minimal coastal organic aerosol production.

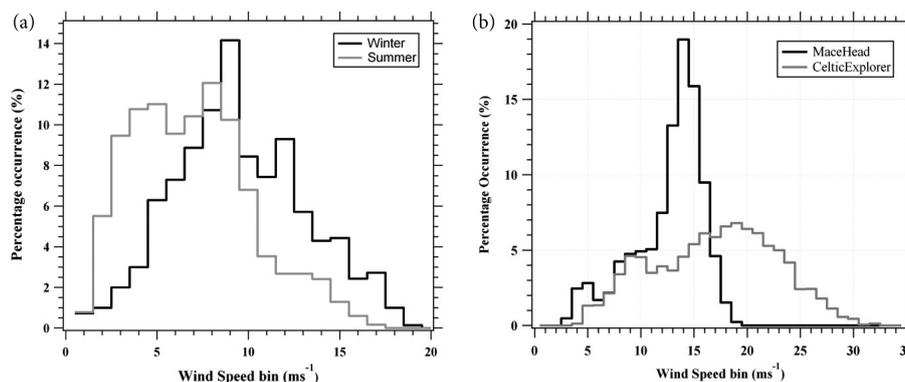


Figure 10. (a) Percentage frequency occurrence distribution for the year 2006 winter and summer seasons. Data reflect hourly averages over 3 months for each season. (b) Percentage frequency occurrence distribution for the *Celtic Explorer* MAP cruise storm offshore from Mace Head (dates: 20–22 June, 2006; latitude: 55–56.5° N; longitude: 9.5–11° W) compared to wind speed measured at Mace Head.

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 metres in the vertical while transported a few kilometres 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 white-capping onset, surf-spray plumes from the upwind island are visible, given the absence of wind-wave breaking surf production, and that these plumes are readily mixed and dispersed vertically. Further, as the wind speed approaches moderate levels of 8 m s⁻¹, the surf plumes produced upwind from Mace Head are increasingly indistinguishable from the breaking wind-wave spray plumes. Given that wind speeds are almost exclusively above the generally accepted whitecap threshold of ~ 4 m s⁻¹ (Monahan, 1971; Callaghan et al., 2008), this would suggest minimal impact of upwind surf plumes on aerosol measured at Mace Head. Figure 10 illustrates the wind speed frequency distribution at Mace Head during the winter (3 months: December, January, February) and summer (3 months: June, July, August) periods. Also shown is a 3-day period of high wind speed about 200 km upwind from Mace Head, measured during the MAP (marine aerosol production) cruise in 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 m s⁻¹, with ~ 15 % of wind speed occurring below the whitecap threshold of 4 m s⁻¹. In winter, while also exhibiting a bimodal structure, the primary peak is at 9 m s⁻¹ and the secondary peak is at 12 m s⁻¹, with a 4 % occurrence below the whitecap threshold. The upstream data during the MAP cruise illustrate the occurrence of a broad

20 m s⁻¹ frequency peak, extending to greater than 30 m s⁻¹ during one particular 2-day summer storm. The simultaneous wind speeds measured at Mace Head exhibit a narrow frequency distribution peak at 14–15 m s⁻¹. The point of this comparison is that there can be, at times, significantly higher winds offshore which potentially could produce sufficient sea spray to dominate over that produced locally at Mace Head, but, in general, wind speed measurements made at Mace Head agree well with the open-ocean wind speed in front of the station, as demonstrated by Gantt et al. (2011). Taking into account the wind speed frequency distribution in conjunction with the analysis in Kunz et al. (2002), one can only conclude minimal influence from offshore breaking surf. Indeed, Kunz et al. (2002) themselves conclude that “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 on 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 a 10 m stretch. In this section, we will address the following questions: is submicron aerosol influenced by the local surf zone at Mace Head and are organic aerosols dominated by coastal contamination?

During the NAMBLEX (North Atlantic Marine Boundary Layer Experiment) experiment, Norton et al. (2006), using micrometeorological measurements, demonstrated some increase in surface drag between the 10 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 strong and could also be attributed to increased drag due to the laboratory buildings which were up to 8 m high and were located at the foot of the tower. During the same experiment, Coe et al. (2006) evaluated the gradient in particle number concentration and non-refractory aerosol chemical species concentration (e.g. nss sulfate, OM, ammonium, etc.) using an AMS switching between two sampling manifolds, sampling from 7 and 22 m heights on the main Mace Head 22 m sampling tower. While some differences were seen in total number concentration and were attributed to shoreline 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 μm 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 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. (2006) height-switching gradient evaluation, which was conducted over a 15 m height difference on short timescales, Ceburnis et al. (2008) conducted gradient flux experiments over an extended 30 m gradient and over timescales 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 footprint. 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. Overall, the gradient method used at Mace Head revealed that the concentration gradient (not the concentration itself) is composed of emissions up to 5 km distant from the measurement location. All sources within that distance, starting from the surf zone and finishing with distant islands, can contribute to the concentration gradient, but the exact contribution of individual sources cannot be deduced from the gradient itself. Only additional estimates or experiments reveal the strength of those sources.

Geever et al. (2005) calculated the flux footprint from the Mace Head 22 m tower as starting ~ 200 m upwind (to the west) of the tower, peaking ~ 800 – 900 m offshore, and extending up to 7–8 km over the water. In contrast, the concentration footprint ranges from 10 to 100 times the flux footprint size, 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 sulfate and 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 sulfate 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. 11), 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 in the clean marine air is indeed associated with POM sea-spray production (rather than long-range transport of pollution); the second is that WIOM can be produced upwind of the flux footprint and is not a surf zone or coastal artefact. The Ceburnis et al. (2008) experiment clearly indicates that at least the WIOM component of OM cannot be exclusively dismissed as a coastal artefact. What about WSOM and sea salt? The gradient profiles always demonstrate a surface source for sea salt, as is to be expected, and never a near-coast surface source for WSOM.

The potential for enhanced coastal primary production 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 three sampling periods from 12 June to 5 July, covering between 36 and 80 h within each of these sampling periods, depending on the sample, with the Research Vessel *Celtic Explorer* operating 200–350 km upwind of Mace Head. The aim of the comparison was not to determine whether what was measured offshore was identical to that measured at Mace Head since such a scenario would represent an unrealistic steady-state scenario between source, evolution, and sink processes over large areas when it is clear that there are differences in both meteorology and ocean-surface composition over such areas. Furthermore, it was to evaluate whether there was a consistently higher mass contribution from particular aerosol chemical species which could be attributed to coastal production artefacts at Mace Head. The comparison cases revealed comparable, if not even higher, offshore concentrations for nss sulfate, WSOM, WIOM, and MSA. Sea salt, in supermicron sizes, exhibited 40 % higher mass at Mace Head, with no discernable differences for submicron sea salt. The whole motivation of this paper is to demonstrate that submicron OM, in particular, originates predominantly from non-surf-zone marine sources. It has previously been shown that breaking surf preferentially produces supermicron salt

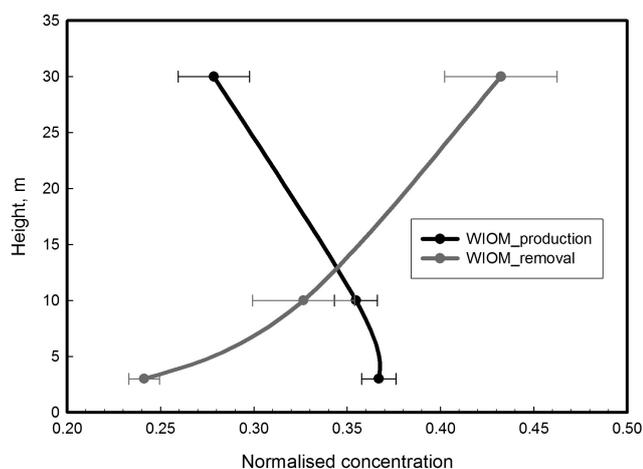


Figure 11. Concentration gradients of PM1 water-insoluble organic matter (WIOM) obtained from 3, 10, and 22 m heights. The positive gradient case represents a surface sink, while the negative gradient with height represents a surface source.

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 for that particular comparison sample. The above studies suggest that there is no discernible 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.

Moreover, 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 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 – those of Martensson et al. (2003), Fuentes et al. (2010b), and Gong (2003) – were applied to predict the resulting mass concentrations for the observed boundary layer height and 2-day wind speed evolution, all of which were found to predict significantly, and unrealistically, higher mass concentrations that resulted in 3–10 times higher concentrations compared to the Mace Head source function. If Mace Head was subjected to notable coastal submicron surf contamination, one might anticipate the actual mass measurements being substantially greater than the predicted values; however, it was exactly the opposite.

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 offshore on the *Celtic Explorer*, and in bubble-bursting laboratory experiments on board the *Celtic Explorer* (Fig. 12). The similarity in the ratio and the size fingerprint

confirms that, at least, the relative proportions of WIOM as a function size are not influenced by coastal artefacts.

3.5 Free-troposphere aerosol

The free troposphere is both a source and a sink of marine boundary layer aerosol via entrainment and detrainment processes and can influence both the microphysics of the size distributions and the physico-chemical properties of the resulting aerosol. Hoell et al. (2000), examined the dominant factors driving the evolution of air masses and aerosol populations as they advected over the Atlantic during the ACE-2 Lagrangian studies and determined, under certain conditions of rapid changes to the boundary layer height (i.e. timescales of less than 24 h), that boundary layer aerosol could be notably diluted or enhanced depending on the BL–FT (boundary layer–free troposphere) gradients. They also acknowledge that the assessment of BL–FT exchange is very complex due to a multi-layer boundary layer structure, as also described in Kunz et al. (2002). For example, taking a typical entrainment rate of 0.5 cm s^{-1} and making the case for the whole well-mixed 1000 m BL air being replaced by a 1000 m FT clean layer (leading to dilution of the BL) or a polluted layer (leading to very notable BL pollution) is not very revealing in terms of source apportionment, due to complex coupling or decoupling of layers within the BL; for the same reason, it is unlikely to be accurate in practice. Nevertheless, entrainment is a reality and can impact on BL or marine aerosol production quantification and physico-chemical characterisation in a number of ways. If the FT is pristine (with negligible anthropogenic/continental influence), the impact on BL aerosol will be mostly to dilute absolute concentrations while maintaining the marine aerosol chemical signature. Size distribution changes are more likely as the FT aerosol is more prone to possess a higher number of smaller particles, contributing relatively more to particle number rather than chemical mass. If the FT aerosol contains polluted layer, such as can be associated with long-range transport of pollution plumes (e.g. anthropogenic or biomass burning related), then the marine aerosol chemical signature will change in conjunction with microphysical or size distribution changes.

If dilution by a pristine FT layer dominates BL–FT exchange, what does this mean for the integrity of marine aerosol characterisation at Mace Head? Given that the marine aerosol burden represents an instantaneous balance between sources and sinks, the characterisation of the aerosol physico-chemical properties can be regarded as representative of marine aerosol for that specific production-loss scenario. On the other hand, if there is a significant aerosol burden in the FT, entrainment of this aerosol will also alter the chemical properties of aerosol measured in the BL. Separating out such a non-marine signature, or isolating the marine component, benefits from sophisticated sampling techniques, such as direct flux measurements, sophisticated

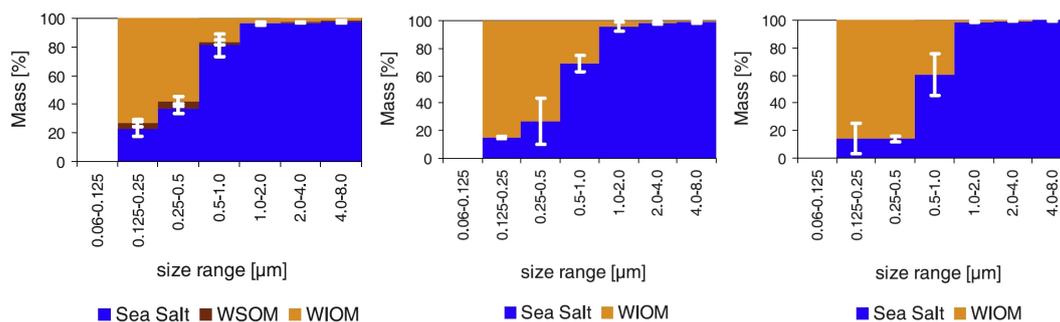


Figure 12. WIOM/sea-salt percentage mass contributions as a function of size for laboratory-based bubble-bursting experiments on the *Celtic Explorer* (left), from air samples collected at Mace Head (middle), and from air samples onboard the RV *Celtic Explorer* (right). Note that while the OM percentage mass contribution illustrates a dominance of OM in submicron sizes, it should be noted that approximately 50 % of the total OM mass resides in the supermicron sizes. Copyright American Geophysical Union (2008); reprinted from Facchini et al. (2008b).

off-line analytical methods such as H-NMR and isotope analysis, or on-line aerosol mass spectrometry. What did such approaches yield in terms of selectively characterising marine aerosol abundance and properties at Mace Head or the contribution of non-marine sources to aerosol measured in the region? Direct fluxes revealed that the WIOM was surfaced-sourced and primary in origin. In addition, the good agreement between fluxes derived from gradient methods and concentration methods suggests that the more extensive concentration-based fluxes are not influenced by entrainment. In terms of chemical fingerprinting or source apportionment, both the HNMR (Decesari et al., 2011) and isotope analysis (Ceburnis et al., 2011) were capable of identifying the non-marine aerosol component, while aerosol mass spectrometry was able to elucidate distinct marine biogenic OM markers and to identify unique marine aerosol tracers of primary marine spray rather than combustion or anthropogenic sources (Ovadnevaite et al., 2011b). Over oceanic regions such as the North Atlantic, boundary layer height is typically 1500 to 2000 m so the trajectories do not necessarily reflect a significant FT entrainment. However, MODIS fire counts for the period presented in Ovadnevaite et al. (2011b) indicated no connection with fires and certainly none over Canada. In addition, HTDMA (Humidity Tandem Differential Mobility Analyser) growth factor measurements revealed organic particles with much lower hygroscopicity than reported in relation to aged forest fire particulate emissions. In terms of distinguishing OM from marine sources from that associated with biomass burning smoke, for example, the marine organic fragmentation pattern was distinctly different from that of aged biomass burning organic aerosol (BBOA) with a coefficient of determination (R^2) between the two mass spectra equal to 0.22. Moreover, major BBOA markers (m/z 60 021 and m/z 73 029), fragments characteristic of levoglucosan (a tracer for cellulose pyrolysis), as well as typical BBOA ion series of C_nH_{2n+1} (m/z 43, 57, 71, etc.; $\Delta = 2$) were all absent in the primary marine OA (organic aerosol), but different fragments such as m/z 39 ($C_3H_3^+$), m/z 53 ($C_4H_5^+$), m/z

43 ($C_2H_3O^+$), m/z 55 ($C_3H_3O^+$), m/z 44 (CO_2^+), and m/z 99 ($C_5H_7O^+$), were prominent. Such a distinct mass spectrum shows a different marine organic plume origin than that of aged BBOA. Aging of BBOA would change the oxidation level of OM; however, there is no indication that it could possibly add new fragments or completely lose the BBOA markers (Jolleys et al., 2012). The use of mass spectral fingerprint analysis to source apportion the marine aerosol arriving at Mace Head suggests that Canadian biomass burning plumes observed over the east coast of North America by Clarke et al. (2007) do not detectably impact on the marine aerosol properties reported under our sampling criteria.

4 Discussion and conclusions

Patterns of biological productivity are different from ocean to ocean; this is especially evident when comparing chlorophyll *a* concentration fields in the contrasting South Pacific and North Atlantic Oceans, the former being more patchy and 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 by $\sim 0.1 \text{ mg m}^{-3}$ with some peak concentrations of 0.4 mg m^{-3} around 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 NE Atlantic summarised in this paper. 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 data sets is that the relationship between OM and BC for BC mass less than 15 ng m^{-3} in Shank et al. (2012) is highly correlated ($R^2 = 0.66$), while neither OM vs. BC, or in this case EBC, 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 and 100 times larger over the Atlantic than 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 intercorrelations, and their relative mass ratios; however, the intercomparison of these parameters point to the conclusion that even OM present at Mace Head (NE Atlantic) at concentrations more than an order of magnitude higher than in the Pacific can be regarded as almost exclusively naturally 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 years, anthropogenic sulfate aerosol concentrations have reduced to 20–25 % of their initial values so that the anthropogenic sulfate contamination of the NE Atlantic has greatly reduced to a similar extent.
- Marine-sector sampling based on wind direction alone is subject to significant anthropogenic contamination from recirculating European continental air; additional criteria such as CN and BC concentrations are required.
- Carbon isotope and HNMR analysis show that $\sim 80\%$ of OM measured at Mace Head according to marine-air criteria is marine biogenic in origin, suggesting an upper limit of 20 % continental and fossil-fuel-sourced total carbon mass.
- Aerosol mass spectral analysis reveals the clear dominance ($\sim 97\%$) of a unique marine POM aerosol type during organic sea-spray plumes.
- Comparison of aerosol-speciated chemical mass at Mace Head and in connected flow upwind and offshore shows no evidence of coastal enhancement of primary aerosol in submicron sizes.
- Gradient measurements between 7 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.

Consolidating the above statements, one can conclude that, for submicron marine aerosol sampled under the Mace Head clean marine air sampling criteria, there are no discernable coastal artefacts and that the anthropogenic contribution to OM associated with marine aerosol under these criteria ranges from 3 % to a maximum of 20 %. The dependency of the anthropogenic contribution to OM as a function of meteorology must be elucidated through further studies on the interaction between marine meteorology and marine biological productivity, ocean-surface water enrichment as a function of wind stress and white capping, temperature influences on sea-spray production, air mass origin, precipitation removal, long-range transport, and changing anthropogenic emissions. Such studies should comprise long-term and continuous measurements of aerosol physicochemical properties, aerosol production and removal, and measurements of both meteorological and biological processes influencing the aerosol life cycle given the dependency of the relative contribution on so many environmental parameters. Such a long-term and continuous measurement programme requires an observation platform fit for purpose, and the arguments presented above, we contend, demonstrate that Mace Head is indeed such a fit-for-purpose platform.

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