**Atmospheric
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On the representativeness of coastal aerosol studies to open ocean studies: Mace Head – a case study

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Abstract. A unique opportunity arose during the MAP project to compare open ocean aerosol measurements with those undertaken at the Mace Head Global Atmosphere Watch Station, a station used for decades for aerosol process research and long-term monitoring. The objective of the present study is to demonstrate that the key aerosol features and processes observed at Mace Head are characteristic of the open ocean, while acknowledging and allowing for spatial and temporal gradients. Measurements were conducted for a 5-week period at Mace Head and offshore, on the Research Vessel Celtic Explorer, in generally similar marine air masses, albeit not in connected-flow scenarios. The results of the study indicate, in terms of aerosol number size distribution, higher nucleation mode particle concentrations at Mace Head than offshore, pointing to a strong coastal source of new particles that is not representative of the open ocean. The Aitken mode exhibited a large degree of similarity, with no systematic differences between Mace Head and the open ocean, while the accumulation mode showed averagely 35% higher concentrations at Mace Head. The higher accumulation mode concentration can be attributed equally to cloud processing and to a coastal enhancement in concentration. Chemical analysis showed similar or even higher offshore concentrations for dominant species, such as nss-SO_4^{-2}, WSOC, WIOC and MSA. Sea salt concentration differences determined a 40% higher supermicron mass at Mace Head, although this difference can be attributed to a higher wind speed at Mace Head during the comparison period. Moreover, the relative chemical composition as a function of size illustrated remarkable similarity. While differences to varying degrees were observed between offshore and coastal measurements, no convincing evidence was found of local coastal effects, apart from nucleation mode aerosol, thus confirming the integrity of previously reported marine aerosol characterisation studies at Mace Head.

1 Introduction

Atmospheric aerosols in the marine environment originate from a combination of primary and secondary sources. The primary component, sea spray aerosol, is produced through physical mechanisms from breaking waves and white caps (Blanchard, 1983; Spiel, 1994, 1997, 1998). The secondary fraction derives from gas-to-particle conversion processes, which involve biogenically emitted precursors, such as dimethyl-sulphide (DMS) (Charlson et al., 1987).

Starting from the 1990s, several studies investigated surf-zone effects in the production of aerosols by means of physical and optical measurements. Aerosol size distributions were investigated by de Leeuw et al. (2000) over the surf zone at two coastal sites in the US by comparing the measurements performed at the base and at the end of a pier in onshore wind conditions. The study demonstrated that the aerosol concentration over the surf increased in the size range between 0.5 and 10 μm, due to local production by breaking waves. However, the authors highlighted that the surf-zone effect was size-dependent, influencing coarse particles more strongly than the submicron size fraction.

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Surf-zone particle production was also investigated at Mace Head, on the west coast of Ireland, during the PAR-FORCE campaign in 1998–1999, by means of lidar scans, finding significant primary aerosol plumes produced by wave breaking in the surf zone and over the open sea (Kunz et al., 2002). During transport to Mace Head, vertical dispersion caused the dilution of primary aerosol, leading the authors to conclude that the influence of these plumes on concentrations measured at Mace Head was relatively small, if any. An attempt to quantify the effect of the plumes was performed by direct measurements at Mace Head (Kleefeld et al., 2002): in good agreement with de Leeuw et al. (2000), submicron aerosol was found to be unaffected by particles produced by wave-breaking.

The above studies, however, do not provide information on the influence of coastal processes on the chemical composition of marine aerosol. From the chemical point of view, the concept of coastal effects can be extended beyond that of enhanced particle production over the wave-breaking zone, including the effect of the coastal biota on aerosol chemical composition. In fact, the coastal biological activity can influence marine aerosol properties through the emission of gaseous precursors or modifying the sea spray composition (Facchini et al., 2008a). In this case the definition of coast relates to a coastal zone of the order of 100 km in extent. O'Dowd et al. (2004) and Cavalli et al. (2004) reported results for the chemical composition of marine aerosol samples collected at Mace Head, providing indirect evidence that the aerosol chemical composition and size distributions observed there were not biased by the proximity of the shoreline nor by the coastal biota (O'Dowd et al., 2004, online supporting material). Simple calculations demonstrated that, assuming both internally and externally mixed marine aerosol, the aerosol organic fraction could only be attributed minimally, if at all, to coastal production. The same authors also reported the results of principal component analysis, eddy-correlation flux measurements and Aerosol Mass Spectrometry gradient measurements, confirming a very low contribution of the shoreline to aerosol number concentration at Mace Head. In a subsequent experiment, Ceburnis et al. (2008) estimated that coastal-generated aerosol might contribute between 5–20% of the aerosol particle mass concentration at Mace Head in the 3–30 m surface layer, but argued that the effect on chemical composition and subsequent chemical fluxes was not significant.

The motivation for this study was to evaluate whether the many exciting results arising from research at the Mace Head Global Atmosphere Watch Station were typical of what would be expected to occur over open oceanic waters, or whether the characteristics of aerosol measured at Mace Head were unique to its coastal environment. To this end, a comparison was made among the number size distribution and size-segregated chemical composition of coastal and open ocean aerosol samples, collected in clean air masses in a period of high biological activity. The objective of this study is not to prove that what is measured at Mace Head is identical to that upwind and over open oceans, as this would require a constraint of no marine aerosol formation and transformation processes. It is more to show that the key aerosol features and processes observed at Mace Head are characteristic of open ocean features and processes, while acknowledging and allowing for spatial and temporal gradients.

2 Experimental set up

The field experiment was carried out as part of the EU Project MAP (Marine Aerosol Production, see http://macehead.nuigalway.ie/map/).

Concurrent measurements were performed from 11 June to 6 July 2006, at the coastal site of Mace Head (MH), Ireland, and over the open ocean onboard the research vessel Celtic Explorer (CE) sailing off the west Irish coast. In this period of the year the phytoplankton bloom typically reaches a maximum in the eastern North Atlantic Ocean. The route of the CE during MAP and the location of MH are shown in Fig. 1. The route of the CE was decided day-by-day in pursuit of highly biologically active sea waters, as monitored by satellite (MODIS). Average chlorophyll-α concentration was $1.4(\pm 0.8)\,\mathrm{mg\,m^{-3}}$ (Facchini et al., 2008a; M., Martino, personal communication, 2007), representative of highly biologically active sea waters.

The investigation of background marine particle properties over the open ocean and at the coastal station was performed by a selective collection of samples in clean marine air masses. These were defined at MH according to the following criteria: the computer-based sampling system ensured only sampling of air (a) reaching the site from a controlled oceanic clean sector between 180 and 300°, (b) having a total particle number concentration below $700\,\mathrm{cm^{-3}}$, and (c) having black carbon concentrations lower than $50\,\mathrm{ng\,m^{-3}}$. Onboard the CE, sampling was performed only when the ship was impacted by westerly air masses. During sampling, the vessel was oriented with the inlets upwind of the funnels of the ship. On-line and post-sampling checking of particle concentrations by a Condensation Particle Counter confirmed the sampling of clean air.

The use of the "clean sector" sampling criterion was necessary to exclude local contamination at MH in order to obtain samples representative of clean marine conditions. Even though some degree of contamination in MH samples cannot be excluded, several evidences collected during the last four years suggest that contaminations are sensibly reduced with the adopted sampling strategy and that the collected samples present a dominant marine character.

Aerosol size distributions at MH were continuously measured by a Scanning Mobility Particle Sizer (SMPS). The scanning time resolution of the SMPS was set to 120 s for mobility particle diameters from 10 to 500 nm. Aerosol was collected through the laminar flow community air sampling system, which has a stainless steel tube of 10 cm diameter
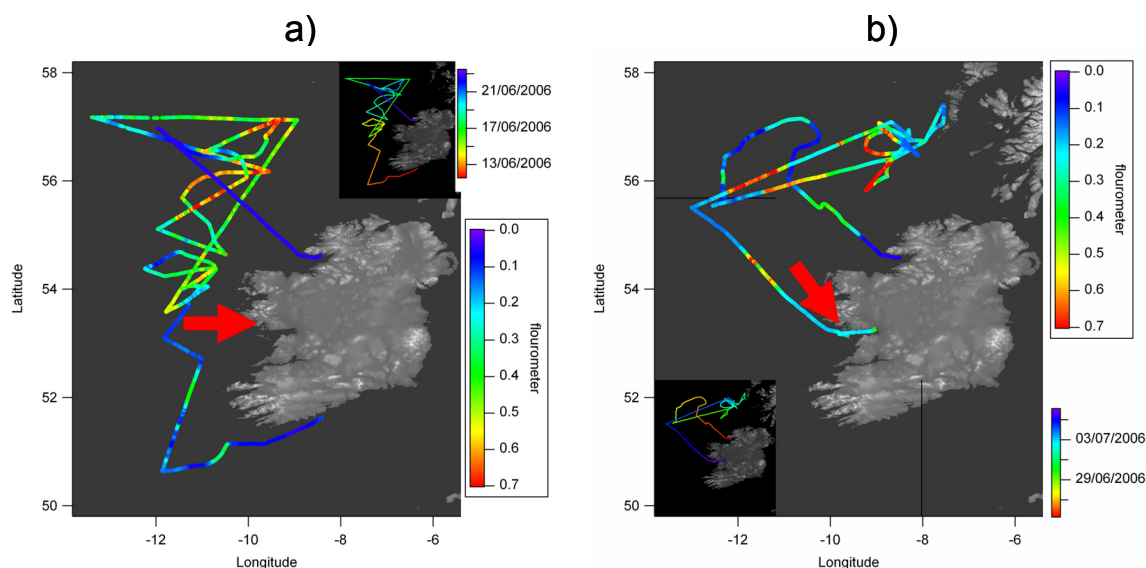
Fig. 1. The Celtic Explorer cruise route (**a**: from 11 to 22 June, **b**: from 25 June to 5 July); the colour of the route in the two large images represents the ship fluorometer signal as a proxy of chlorophyll-α concentration (in the smaller inserted images they refer to the date, see the appropriate scale). The red arrows indicate the location of the Mace Head Research Station.

and an inlet 10 m above the ground. Onboard the CE, the particle number size distribution was measured by a twin Differential Mobility Particle Sizer (DMPS), installed in a container mounted on the front deck (sampling height was ~14 m a.s.l.). One of the DMPS operated in the 3–50 nm particles size range, the other in the 15–950 nm size range; the operating time resolution was of 10 min. During analysis, the data were combined to obtain the total number size distribution of 3–950 nm particles.

At both sites aerosol samples for chemical analyses were collected by means of 8-stage Berner impactors equipped with tedlar foils, collecting particles in eight size fractions between 0.06 and 16 μm diameter (cut-offs: 0.06, 0.125, 0.25, 0.50, 1.0, 2.0, 4.0, and 8.0 μm at 50% efficiency). To obtain a more comprehensive chemical characterization of the organic fraction, aerosol samples were also collected in parallel by high volume cascade impactors, segregating fine (aerodynamic diameter smaller than 1.5 μm) and coarse particles (aerodynamic diameter between 1.5 and 10 μm diameter) on quartz filters. At the coastal site, the impactor sampling was performed on a tower (10 m height), while the high volume sampling was carried out at ground level (1.5 m); both samplers operated in open air. On the ship, both samplers were placed in open air on a port side of the ship (which was aimed at the angle to the wind) to minimize any contamination from ship stacks, at approximately 14 m a.s.l.

High volume samples were collected at MH using a back-up filter in series with the fine filter (quartz behind quartz approach), in order to evaluate the contribution of positive sampling artifacts. For the CE samples, the artifact correction was performed assuming the same average front/back-up

Table 1. Aerosol sampling schedule at Mace Head (MH) and onboard the Celtic Explorer (CE).

Sample	Start date	Stop date	Time of sampling (h)
MH1	12 Jun 2006	19 Jun 2006	80.3
CE1	12 Jun 2006	15 Jun 2006	64.0
MH2	19 Jun 2006	28 Jun 2006	50.0
CE2	16 Jun 2006	20 Jun 2006	57.2
MH3	28 Jun 2006	05 Jul 2006	36.0
CE3	26 Jun 2006	04 Jul 2006	59.7

filter ratio obtained for the MH samples. Three parallel aerosol samples were collected during the campaign for about 50 h each (see Table 1).

Analyses of aerosol inorganic components and water soluble organic carbon (WSOC) were performed on tedlar foils (Matta et al., 2003; Cavalli et al., 2004). The uppermost impactor stage (8.0–16.0 μm) was not analyzed, because of the very low collection efficiency of the impactor inlet at wind speed of 5 m s^{-1} and above (Howell et al., 1998). Aliquots of the high volume samples were analysed for Total Carbon (TC) and WSOC.

The WSOC and TC analyses were performed using a Multi N/C 2100 elemental analyser (Analytik Jena, Germany), equipped with a furnace solids module. For WSOC analyses, tedlar foils or aliquots of the quartz fibre filters were extracted in a small volume of ultra-pure milli-Q water

Table 2. Overall mean relative random uncertainties for each aerosol component; uncertainties are given as percentages.

size range (µm)	nss-SO_4^{-2}	sea salt	NH_4^+	NO_3^-	MSA	WSOC	WIOC
0.06–0.125	7	70	25	–	6	28	
0.125–0.25	6	106	6	–	6	13	
0.25–0.5	6	38	6	–	6	10	
0.5–1.0	6	9	6	50	6	13	
1.0–2.0	6	6	7	8	6	14	
2.0–4.0	6	6	10	10	6	14	
4.0–8.0	6	6	8	10	6	22	
<1.5							19
1.5–10							17

by 30 min sonication. Extracts obtained from high volume samples were filtered by PTFE filters (Sartorius, Germany) in order to remove quartz fragments. Extracts were analysed using the same instrumental setup described in Rinaldi et al. (2007). For TC analyses, a small portion of exposed quartz filters (1.3 cm^2) was introduced into the instrument furnace for thermal analysis. Inside the combustion chamber the sample was exposed to a constant temperature of 950 °C in a pure oxygen atmosphere, in the presence of a catalyst (CeO$_2$). Under such conditions all carbonaceous matter (organic carbon, carbonate and elemental carbon) evolves to CO$_2$. The TC was determined as the total evolved CO$_2$ by a non-dispersive infrared (NDIR) detector. The instrumental detection limit was 0.2 µg of carbon and the accuracy of the TC measurement was better than 5% for 1 µg of carbon. The water insoluble organic carbon (WIOC) was calculated as the difference between TC and WSOC.

Proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy was employed for functional group analysis of WSOC extracted from high volume samples as described in Cavalli et al. (2004). The WSOC was converted to water-soluble organic mass (WSOM) using a factor of 1.8, based on the functional group composition of WSOC (see Sect. 3.3). A conversion factor of 1.4 was instead applied to convert WIOC to water-insoluble organic mass (WIOM), according to the functional group composition observed by H NMR in sea spray organic aerosols (Facchini et al., 2008a). Sea salt and nss-SO_4^{-2} aerosol concentrations were calculated using Na$^+$ as sea salt tracer and a standard sea salt composition (Seinfeld and Pandis, 1998).

The random uncertainty for each aerosol component and each size range was computed using the procedure of error propagation described by Putaud et al. (2000), including: (1) uncertainty in the sampled air volume, ±3% for Berner impactors and ±10% for high volume samplers; (2) precision of the extraction water volume, ±0.04 mL; (3) uncertainties in ion chromatography, WSOC and TC measurements, ±5%; and (4) the blank variability. For correlated parameters, absolute uncertainties were added conservatively. The mean relative random uncertainties for all aerosol component concentrations are reported in Table 2.

2.1 Back-trajectory analysis

The 48-h backward trajectories were calculated, using the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT model (Draxler and Rolph, 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (see http://www.arl.noaa.gov/ready/hysplit4.html), NOAA Air Resources Laboratory, Silver Spring, MD), every 12 h for all the campaign. Back-trajectories with endpoints at MH and CE typically originated in the same area of the Atlantic Ocean, with 73% of the pairs of trajectories appearing as streamlines of the same regional flow intercepting both MH and the CE. Usually, the two sampling sites were characterised by parallel streamlines spaced by 50–100 km. Most of the back-trajectories highlighted the main atmospheric circulation patterns encountered during the campaign, which can be classified into: (a) North Atlantic cyclonic air masses together with Greenland and Arctic air masses and (b) mid Atlantic air masses (coming from the West and South-West). The back-trajectory analysis confirms that the aerosol samples collected at the two sites are representative of the same sources, processes and sinks, with the exception that aerosols collected at Mace Head have been transported over the coastal zone before sampling. Examples of back-trajectories, together with the average chlorophyll-α concentration over the North Atlantic during the campaign period, are reported in Fig. 2.

3 Results and discussion
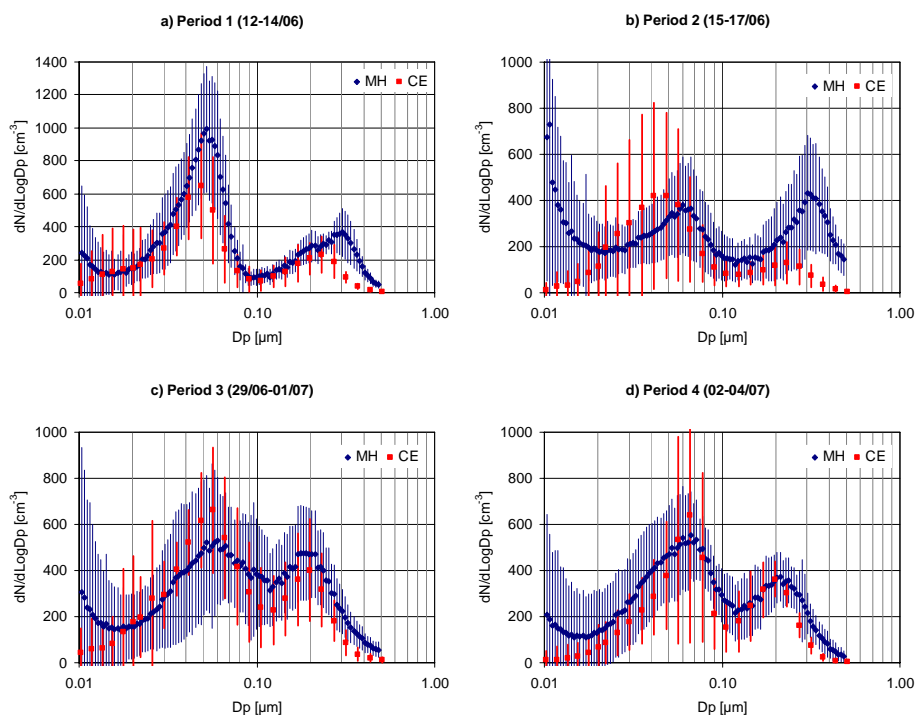
3.1 Aerosol number size distribution

For the size distribution comparison, the campaign period has been divided into four sub-periods characterised by homogeneous air mass origin and good trajectory agreement between MH and the CE, based on the back-trajectory analysis (see Sect. 2.1). Only data collected within the clean sector (see Sect. 2), both at MH and onboard the CE, were used. All the periods during which measurements were not available at both sites were excluded from the analysis.

Figure 3 shows the average number size distributions measured at MH and onboard the CE during the four sub-periods; ±1 standard deviation bars have been plotted to show the variability of the average value. The number size distributions reported in Fig. 3 present the typical features of remote marine aerosol populations, with two modes in the 0.02–1 µm size range: the Aitken mode and the accumulation mode (Heintzenberg et al., 2000). Particle number concentrations and mean modal diameters are consistent with the results obtained by other investigators (Jensen et al., 1996), and agree with previous measurements performed at MH in the same period of the year (Yoon et al., 2007).
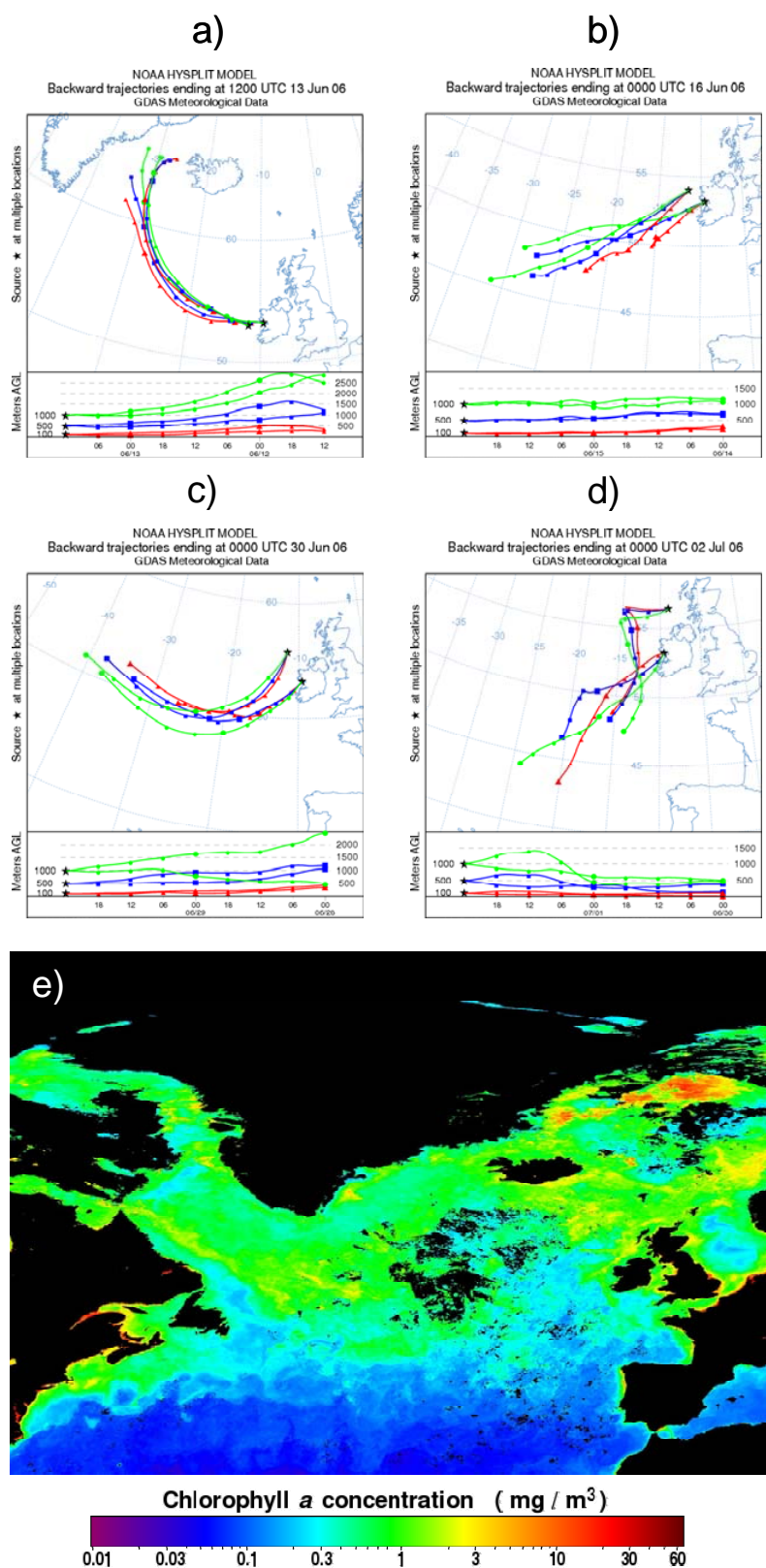
Fig. 2. Examples of back-trajectories for the periods **(a)** 12–14 June, **(b)** 15–17 June, **(c)** 29 June–1 July, **(d)** 2–4 July, and **(e)** average chlorophyll-α concentration over the North Atlantic during the campaign. Trajectories were produced with HYSPLIT from the NOAA ARL website (http://www.arl.noaa.gov/ready/), the stars indicate Mace Head and the Celtic Explorer position. The chlorophyll map was obtained by level 3 products taken from MODIS (http://oceancolor.gsfc.nasa.gov/).
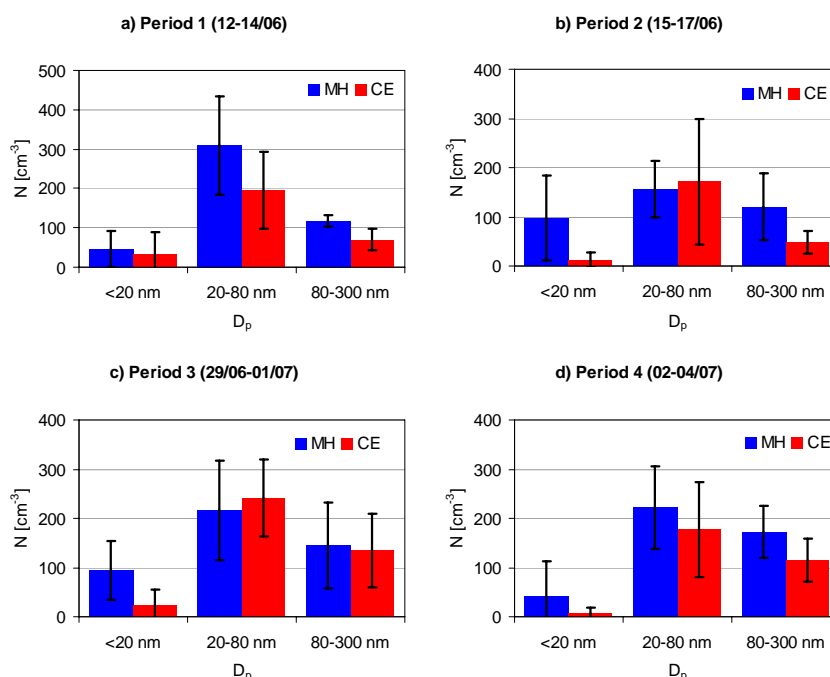
Fig. 3. Average aerosol number size distributions measured at Mace Head (MH) and over the open ocean (CE): **(a)** 12–14 June, **(b)** 15–17 June, **(c)** 29 June–1 July and **(d)** 2–4 July. Bars represent ±1 standard deviation.

A general agreement can be observed between number size distributions measured at MH and over the open ocean. The main difference between the spectra is in the nucleation mode ($D_p < 20$ nm), which clearly exhibits higher concentrations at Mace Head compared to offshore concentrations, pointing to a stronger coastal source of new particles that is not representative of the open ocean. In spite of the very high contribution in terms of particle number, freshly nucleated particles cannot affect the aerosol chemical composition in the investigated size ranges because of their negligible contribution to the total mass. Moreover, a full discussion of nucleation events at the coastal site and over the open ocean is beyond the scope of the present work. Therefore, differences in the nucleation mode particle number will be not discussed in detail below.

To perform a quantitative comparison, coastal and open ocean number size distributions are discussed in terms of particle number in the Aitken ($20 < D_p < 80$ nm) and accumulation mode ($80 < D_p < 300$ nm). Figure 4 shows the average particle number measured at MH and onboard the CE during the four sub-periods. The Aitken mode exhibited a large degree of similarity with no systematic differences between MH and the CE; the average difference, expressed with respect to MH number concentration, ranged from –37% to +12%. Accumulation mode showed averagely a 35% higher particle number concentration at Mace Head. The maximum difference was observed during period 2, when a difference of 72 particles per cc was observed between MH and the CE,

accounting for 60% of MH accumulation mode particle concentration. During periods 1, 3, and 4 the difference with respect to MH was 40, 7, and 34%, respectively.

Even though the experiment was not conducted in connected-flow conditions, that is MH was not always directly downwind to the CE, it is reasonable to assume that coastal particles represent, on average, a more processed aerosol population than open ocean particles in westerly wind conditions. Therefore, the systematically higher accumulation mode coastal concentration can be, at least partly, attributed to aerosol processing. According to our calculations, based on the approach of O'Dowd et al. (2000), in-cloud heterogeneous oxidation was the only mechanism capable of producing the observed growth, from Aitken to accumulation mode, in the short time scale characterizing the advection of aerosol from 300 km offshore to the coast (∼10 h). Particularly, cloud processing can be invoked in sub-periods 2 and 3, when the Aitken mode particle number was higher over the open ocean than at MH, while the accumulation mode particle number was higher at MH, suggesting a shift in particle size during the advection from the open ocean to the coast. Even though some costal influence can have contributed to the systematically higher accumulation mode particle number at the coastal site, the magnitude of the difference is not large enough (averagely 35%) to demonstrate a substantial bias of aerosol size distributions measured at Mace Head due to coastal processes.

Fig. 4. Average aerosol number concentrations in nucleation ($D_p < 20$ nm), Aitken ($20 < D_p < 80$ nm) and accumulation ($80 < D_p < 300$ nm) mode measured at Mace Head (MH) and over the open ocean (CE): **(a)** 12–14 June, **(b)** 15–17 June, **(c)** 29 June–1 July, and **(d)** 2–4 July. Bars represent ± 1 standard deviation.

Table 3. Average atmospheric concentration (μg m^{-3}) and nss-SO$_4^{-2}$-normalized concentration of the main aerosol components; standard deviation of the mean value is reported in brackets. "Fine" refers to particles smaller than 1.5 μm for WIOC and smaller than 1 μm for other species. "Coarse" refers to particles between 1.5 and 10 μm for WIOC and between 1 and 8 μm for other species.

|	Fine		Coarse		nss-SO$_4^{-2}$-normalized (Fine)	
	MH	CE	MH	CE	MH	CE
nss-SO$_4^{-2}$	0.39 (0.08)	0.45 (0.16)	0.09 (0.05)	0.06 (0.04)	–	–
NH$_4^+$	0.06 (0.01)	0.06 (0.02)	0.001 (0.002)	0.003 (0.005)	0.15 (0.01)	0.17 (0.01)
NO$_3^-$	0.002 (0.003)	0.001 (0.002)	0.18 (0.09)	0.13 (0.09)	0.006 (0.01)	0.003 (0.005)
sea salt	0.07 (0.02)	0.07 (0.04)	4.21 (0.54)	3.00 (0.81)	0.16 (0.04)	0.16 (0.03)
WSOC	0.13 (0.03)	0.14 (0.05)	0.09 (0.06)	0.07 (0.02)	0.34 (0.06)	0.32 (0.02)
WIOC	0.05 (0.01)	0.08 (0.01)	0.07 (0.03)	0.04 (0.02)	0.14 (0.02)	0.19 (0.05)
MSA	0.11 (0.02)	0.17 (0.06)	0.09 (0.03)	0.08 (0.03)	0.29 (0.07)	0.38 (0.04)

3.2 Marine aerosol chemical composition

Given the difficulties in coordinating the automated clean marine sector sampling at Mace Head with the offshore sampling, aerosol samples were not collected at coinciding sampling intervals at the two sites (see Table 1). Therefore, the coastal and open ocean aerosol chemical composition is discussed only in terms of average concentrations, obtained by averaging the three time-integrated samples collected at each sampling site during the campaign. Using this approach, concentrations representative of summer conditions over the East North Atlantic Ocean and at Mace Head were obtained for the main aerosol components, able to

evidence systematic differences in the aerosol chemical composition between the two sites.

Figure 5 shows a comparison of main aerosol components average size segregated atmospheric concentration at MH and over the open ocean, while Table 3 reports the average submicron and supermicron concentrations. A generally good agreement can be observed between the average mass size distributions of the main aerosol components measured over the open ocean and at MH. The non-sea-salt sulphate (nss-SO$_4^{-2}$) (Fig. 5a) mass size distribution exhibits a principal mode in the 0.25–0.5 μm stage in both data sets. In addition, a second minor mode, corresponding to the 2.0–4.0 μm size range, is present, more
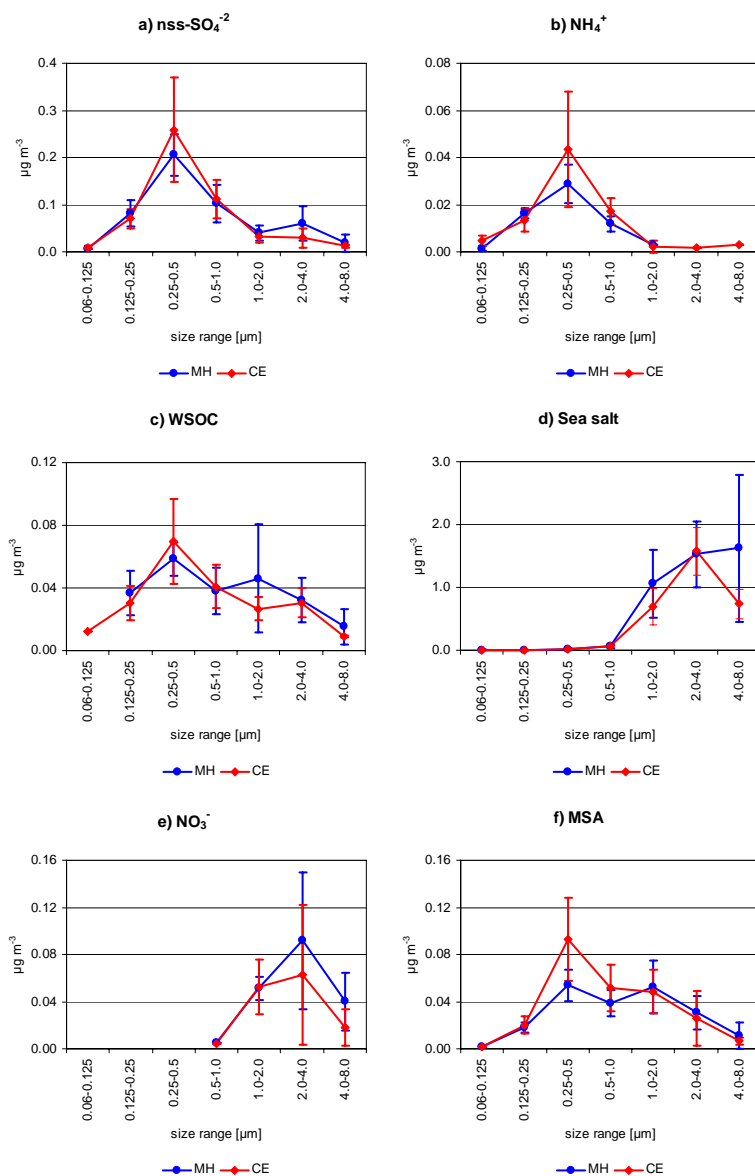
Fig. 5. Average mass size distribution of the main aerosol components measured on impactor samples at Mace Head (MH) and onboard the Celtic Explorer (CE). Bars represent ±1 standard deviation.

markedly at MH. Submicron concentrations of nss-SO_4^{-2} as $0.39(\pm0.08)\,\mu g\,m^{-3}$ and $0.45(\pm0.16)\,\mu g\,m^{-3}$ were measured at MH and over the open ocean, with the greater part of the difference in the fine accumulation mode (0.25–0.5 μm). A mass size distribution similar to that of nss-SO_4^{-2} was observed for NH_4^+ at both sites, with supermicron concentrations often below or very close to the detection limit. The submicron NH_4^+ concentration was always below the remote marine background concentrations reported by Jickells et al. (2003). Submicron WSOC concentrations were $0.13(\pm0.03)\,\mu g\,m^{-3}$ and $0.14(\pm0.05)\,\mu g\,m^{-3}$ at MH and onboard the CE, while supermicron concentrations were $0.09(\pm0.06)\,\mu g\,m^{-3}$ and $0.07(\pm0.02)\,\mu g\,m^{-3}$.

The sea salt mass size distribution was similar at MH and over the open ocean, with about 50 times more mass in the supermicron range than in the submicron one. The average sea salt concentration (Table 3) was 1.4 times higher at MH with respect to the open ocean in the 1.0–8.0 μm size range. Observing the plot in Fig. 5d, it is clear that most of the difference is due to the mass contribution of the largest size range (4.0–8.0 μm). Fine sea salt reveals a different behaviour, having similar concentrations in CE and MH samples (difference of 5%, within the random uncertainty range). Nitrate (NO_3^-) was detected in all samples in the coarse mode, with a size distribution resembling that of sea salt.

The WIOC average atmospheric concentrations, measured on the high volume filters (Fig. 6), present a different size distribution at MH and on the open ocean: the average fine WIOC concentration at MH is 0.62 times that measured over the open ocean, while in the coarse fraction, the average concentration at the coastal site is 1.8 times the one onboard the CE. Over the open ocean, the concentration of WIOC in the fine mode is $2.7(\pm1.4)$ times that of the coarse mode, while in the coastal samples the ratio between the two modes is $0.9(\pm0.3)$.

The possible effects of coastal processes can be investigated by comparing the difference in concentration of a given chemical constituent between MH and CE with that of species whose formation processes are known. $NssSO_4^{-2}$ can be used as a reference species because it is produced in the marine boundary layer by secondary sources spread over wide oceanic regions with little impact from coastal processes. The ratio in the size-segregated concentrations of nss-SO_4^{-2} in submicron impactor stages between MH and the CE ranges between 0.8 and 1.2. Following this approach, ratios within this range for any aerosol component have been considered as due to differences in air mass characteristics or to sampling and analysis uncertainty, while ratios exceeding this range must be explained by physical or chemical processes related to the proximity of the surf zone at the coastal sampling site. Only submicron MSA (discussed in the next paragraph) and WIOC showed negative anomalies (respectively 0.7 and 0.6) compared to nss-SO_4^{-2}, pointing to stronger open ocean sources. By contrast, the coarse aerosol chemical components showed positive anomalies ($Conc_{MH}/Conc_{CE} > 1.2$), suggesting that the shorter lifetime of coarse particles makes them more subjected to coastal effects. The difference in coarse sea salt ($Conc_{MH}/Conc_{CE}$ ratio of 1.4), in particular, may be the result of the higher wind speed measured at MH during the campaign (average wind speed over the sampling period at the coastal site was $1.8(\pm0.4)$ times that measured over the open ocean). In Table 3, we reported the concentrations of submicron aerosol chemical components normalized by nss-SO_4^{-2}, in order to remove the effect of possible biases in total aerosol concentrations caused by non coincidental air flow between the two stations. No net increase of the main submicron aerosol species at MH with respect to the CE was observed: the differences in the nss-SO_4^{-2}-normalized concentrations in submicronic aerosols between CE and the MH are +14%, +0.1%, −7%, +32%, and +26% for NH_4^+, sea salt, WSOC, WIOC and MSA, respectively. It must be noted that the two main differences, observed for WIOC and MSA, have opposite sign with respect to the expected coastal effect, i.e. the highest concentrations are found in the open ocean.

Using a similar approach, we normalized the size-segregated concentrations of the chemical species by their sum in each size intervals, providing normalized concentrations also for the constituents of the coarse mode, where the nss-SO_4^{-2} concentrations are very low. Figure 7 reports the
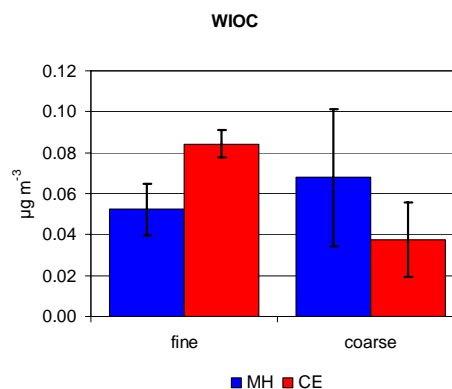

Fig. 6. Average aerosol WIOC concentration in fine ($D_p < 1.5\,\mu m$) and coarse ($D_p > 1.5\,\mu m$) size ranges measured at Mace Head (MH) and onboard the Celtic Explorer (CE). Bars represent ±1 standard deviation.

size-segregated chemical composition of the aerosol samples collected at MH and onboard the CE averaged over the whole campaign. The size-resolved mass fractions for water insoluble organics were extrapolated from the high volume data, using the same procedure as Cavalli et al. (2004).

Figure 7 shows that the "chemical fingerprint", i.e. the size segregated fractional contribution of dominant chemical species, is practically identical for Mace Head samples and off-shore samples, with all the component contributions agreeing within 5%. These results are the first direct observations that the chemical composition of marine aerosol observed at MH during the summer period is not affected by any local coastal influence.

At both sites, the main components of the fine aerosol fraction are nss-SO_4^{-2} and WSOM (WSOM = WSOC × 1.8). The former accounts for 44 ± 6 and $45\pm1\%$ of the fine aerosol mass at the coastal site and open ocean, respectively, while the latter contributes 27 ± 6 and $26\pm2\%$ at MH and on the CE, respectively. In contrast with observations during previous campaigns at MH (Cavalli et al., 2004; O'Dowd et al., 2004), water insoluble organic matter (WIOM = WIOC × 1.4) accounts for only 8 ± 0.1 and $12\pm3\%$ of the fine aerosol mass at MH and CE, respectively. As expected, sea salt dominates the chemical composition of the coarse aerosol fraction in both data sets ($89\pm5\%$ and $90\pm2\%$ of the submicron mass at MH and onboard CE, respectively).

The WSOC and nss-SO_4^{-2} concentrations show a statistically significant correlation (P<0.01) in both data sets (r=0.84 for MH and 0.97 for CE), suggesting a formation pathway for WSOC similar to that of nss-sulphate, i.e. gas-to-particle conversion from biogenic volatile organic precursors. A secondary formation route for WSOC is also supported by the findings of a recent experiment performed at MH, in which gradient fluxes of sea salt, nss-SO_4^{-2}, WSOC and WIOC were calculated (Ceburnis et al., 2008). During the said experiment, upward fluxes indicative of emission
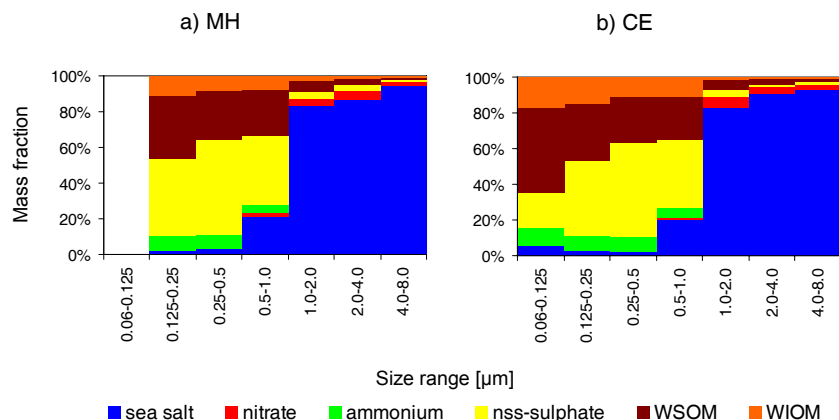
Fig. 7. Average relative chemical composition of coastal (MH) and open ocean (CE) aerosols. The aerosol chemical composition in the size range 0.06–0.125 μm is not shown for MH, since the concentration of organics was below detection limit for all three samples (the detection limit for organics is about one order of magnitude higher than that of inorganic ions due to different instrumental sensitivity and different field blank values).

from the sea-surface (primary formation) were found for sea salt and WIOC, whereas downward fluxes characteristic of chemical species forming through secondary processes were measured in the cases of nss-SO_4^{-2} and WSOC.

Along with the results of Ceburnis et al. (2008), recent experiments have shown that WIOC and sea salt are the main sea spray components (Facchini et al., 2008a). The relative contribution of WIOM and sea salt to sea spray was similar in the two data sets: only 2% of sea spray mass was organic in the coarse fraction of both data sets, indicating that the wave-breaking zone effect did not influence the relative enrichment of organic and inorganic components of sea spray. Fine sea spray mass was 54%(±10%) and 63%(±12%) organic at MH and over the ocean, respectively. Such compositions are within the range of variability reported by O'Dowd et al. (2008) for submicron sea spray during the period of high biological activity in the North Atlantic. The higher organic contribution found in fine open ocean sea spray particles can be attributed to the influence of more biologically active open ocean waters. Satellite derived chlorophyll-a maps confirm a patchy distribution of chlorophyll over the North East Atlantic, with open ocean spots often more productive than coastal waters (Yoon et al., 2007).

3.3 Characterization of the organic fraction

Methanesulfonic acid (MSA) was the main organic compound detected in the impactor and filter samples collected during MAP. Figure 5f reports the average MSA size distribution for coastal and open ocean samples. The MH average mass size distribution exhibits comparable MSA concentrations in the fine and coarse mode, with mass peaks in the 0.5–1.0 and 1.0–2.0 μm size ranges. Conversely, the open ocean MSA size distribution peaks neatly in the accumulation mode (0.25–0.5 μm). Submicron MSA concentration

was $0.17(\pm0.06)\,\mu g\,m^{-3}$ against $0.11(\pm0.02)\,\mu g\,m^{-3}$ measured at MH.

We observed a 40% excess of MSA concentrations in the 0.25–0.5 μm size range measured on board the CE compared to MH. We hypothesize that the higher concentration of accumulation mode MSA measured over the open ocean results from the transit of air masses over more biologically productive waters, as discussed above, or, alternatively, from the oxidation of MSA to nss-SO_4^{-2} during transport to the coast. The latter hypothesis is supported by the higher submicron nss-SO_4^{-2}/MSA mass ratio measured at MH (3.56±0.76) with respect to the open ocean (2.68±0.32). The presence of more oxidized sulphur species can be interpreted as evidence that coastal particles are more processed (aged) than those collected over the ocean, as discussed in Sect. 3.1. The difference in the nss-SO_4^{-2}/MSA ratio is less pronounced in the coarse size range, which is consistent with effects of a relatively shorter atmospheric lifetime of the supermicron particles.

The functional group composition of WSOM in the submicron size fraction was investigated using ^{1}H NMR spectroscopy. Figure 8 shows the functional group distributions for coastal and open ocean samples together with that of a polluted aerosol sample collected at Mace Head in HBA conditions. The sample sets collected in clean marine air masses at MH and on the CE exhibit similar water-soluble organic functional group distributions, with large contributions from MSA (from 11 to 34% of total μmolH m^{-3}) and amine (H-C-N) groups (from 2 to 7% of total μmolH m^{-3}), in contrast to the sample collected during the outbreak of polluted continental air masses, which is depleted of MSA and, especially, amines. Another difference is that the polluted aerosol sample shows a higher aromatic character (5%), consistently with what already observed in other polluted European sites, in contrast to the samples of clean marine air, in which the
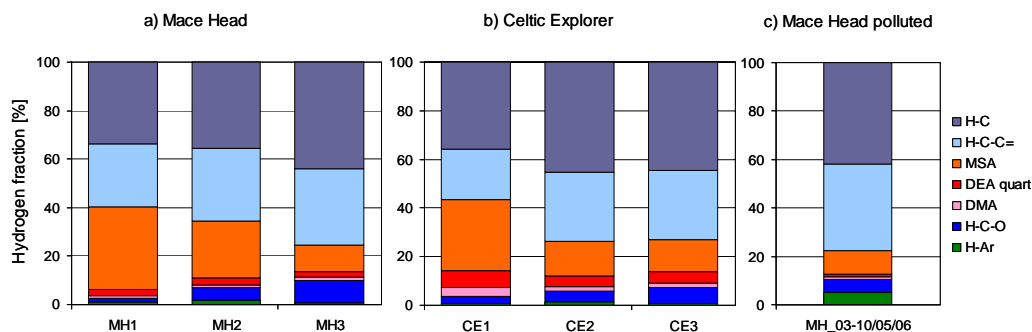
Fig. 8. Functional group relative composition of WSOC in Mace Head **(a)** and Celtic Explorer **(b)** samples. For comparison, the functional group composition of the sample collected in the period 3–10 May 2006, in continental influence conditions, has been reported **(c)**. H-Ar, aromatic protons; H-C-O, protons bound to oxygenated aliphatic carbon atoms; H-C-N, protons bound to aliphatic carbon atoms bearing nitrogen atoms; MSA, methansulphonate; H-C-C=, protons bound to aliphatic carbon atoms adjacent to unsaturated groups; H-C, purely alkylic protons.

particulate aromatic compounds occur only in trace amounts. The presence of amines, which are organic compounds of clear secondary origin (Facchini et al., 2008b), supports our finding that secondary biogenic sources account for a large fraction of WSOA in the north-east Atlantic and that are therefore related to open ocean sources rather than to coastal emissions.

Finally, a higher contribution of purely alkylic groups (C-H) can be observed in CE samples with respect to MH ones. The ratios between oxygenated (H-C-C=O+H-C-O) and non-oxygenated (C-H) aliphatic functional groups were 0.91 ± 0.09 and 0.73 ± 0.07 for MH and CE, respectively. Combined with the above results for MSA and inorganic ion concentrations, the latter finding suggests that aerosol particles undergo oxidation during the advection to the Irish coast.

4   Conclusions

This study compares simultaneous measurements of aerosol chemical composition and number size distribution in strictly controlled clean marine air at Mace Head and at various locations off the Irish coast and examines resulting aerosol properties in terms of elucidating any possible local coastal influence.

In terms of aerosol physical properties, the nucleation mode clearly exhibited elevated concentrations at Mace Head compared to offshore concentrations, pointing to a strong coastal source of new particles that is not representative of the open ocean. The Aitken and accumulation modes showed, instead, lower differences between the coastal and the open ocean sampling sites, with the Aitken mode exhibiting a larger degree of similarity with no systematic differences between Mace Head and the open ocean. Accumulation mode presented systematically higher concentrations at Mace Head (averagely 35%). The systematically higher accumulation mode concentration can be attributed equally to

cloud processing and to a coastal enhancement in concentration, although the difference is not large enough to demonstrate a substantial bias of aerosol size distributions measured at Mace Head due to coastal processes.

Aerosol main chemical components showed similar mass size distributions at the coastal site and over the open ocean, with concentration differences between the two sites comparable with those of submicron non-sea-salt sulphate (for which it is reasonable to assume no coastal influences) with few exceptions. Moreover, the resulting relative chemical composition as a function of size of coastal and open ocean samples showed a remarkable similarity, resulting in the same "chemical fingerprint" for coastal and open ocean aerosols. In addition, the detailed chemical characterization of the marine aerosol water soluble organic fraction showed similarity of composition for coastal and offshore sampled organic aerosols, even though a more oxidized character was evident in coastal samples.

In conclusion, while differences to varying degrees were observed between offshore and coastal measurements at Mace Head, no significant evidence was found for local coastal influences during the campaign period, apart from nucleation mode aerosol, which clearly has a coastal source. Therefore, marine aerosol properties, particularly the "chemical fingerprint", measured at a height of 10 m, or higher, under strictly controlled clean marine sector conditions at Mace Head can be considered representative of marine aerosol sampled over the East North Atlantic within about 300 km from the Irish coast, at least in conditions comparable with those met during the campaign.

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References

Blanchard, D. C.: The production, distribution, and bacterial enrichment of the sea-salt aerosol, in: Air-Sea Exchange of Gases and Particles, edited by Liss, P. S. and Slinn, W. G. N., D. Reidel, Norwell, MA, 407–454, 1983.

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., 109, D24215, doi:10.1029/2004JD005137, 2004.

Ceburnis, D., O'Dowd, C. D., Jennings, G. S., Facchini, M. C., Emblico, L., Decesari, S., Fuzzi, S., and Sakalys, J.: Marine aerosol chemistry gradients: elucidating primary and secondary processes and fluxes, Geophys. Res. Lett., 35, L07804, doi:10.1029/2008GL033462, 2008.

Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate, Nature, 326, 655–661, 1987.

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.

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, 2008a.

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(24), 9116–9121, 2008b.

Heintzenberg, J., Covert, D. C., and Van Dingenenn, R.: Size distribution and chemical composition of marine aerosols: a compilation and review, Tellus B, 52, 1104–1122, 2000.

Howell, S., Pszenny, A. A. P., Quinn, P., and Huebert, B.: A field intercomparison of three cascade impactors, Aerosol Sci. Technol., 29, 475–492, 1998.

Jensen, T. L., Kreidenweis, S. M., Kim, Y., Sieverinag, H., and Pszenny, A.: Aerosol distributions in the North Atlantic marine boundary layer during Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange, J. Geophys. Res., 101(D2), 4455–4467, 1996.

Jickells, T. D., Kelly, S. D., Baker, A. R., Biswas, K., Dennis, P. F., Spokes, J., Witt, M., and Yeatman, S. G.: Isotopic evidence for a marine ammonia source, Geophys. Res. Lett., 30(7), 1374, doi:10.1029/2002gl016728, 2003.

Kleefeld, C., O'Reilly, S., Jennings, S. G., Kunz, G. J., de Leeuw, G., Aalto, P., Becker, E., and O'Dowd, C. D.: The relative contribution of sub and super micron particles to aerosol light scattering on the marine boundary layer (MBL), J. Geophys. Res., 107(D19), 8103, doi:10.1029/2000JD000262, 2002.

Kunz, G., de Leeuw, G., O'Dowd, C. D., and Becker, E.: Lidar studies of the atmospheric boundary layer and locally generated sea spray aerosol plumes at Mace Head, J. Geophys. Res., 107, 8106, doi:10.1029/2001JD001240, 2002.

Matta, E., Facchini, M. C., Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Putaud, J.-P., and Dell'Acqua, A.: Mass closure on the chemical species in size-segregated atmospheric aerosol collected in an urban area of the Po Valley, Italy, Atmos. Chem. Phys., 3, 623–637, 2003,
http://www.atmos-chem-phys.net/3/623/2003/.

O'Dowd, C. D., Lowe, J. A., and Smith, M. H.: The effects of clouds on aerosol growth in the rural atmosphere, Atmos. Res., 54(4), 201–221, 2000.

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, 2004.

O'Dowd, C. D., Langmann, B., Varghese, S., Scannell, C., Ceburnis, D., and Facchini, M. C.: A combined organic-inorganic sea-spray source function, Geophys. Res. Lett., 35, L01801, doi:10.1029/2007GL030331, 2008.

Putaud, J.-P., Van Dingenen, R., Mangoni, M., Virkkula, A., Raes, F., Maring, H., Prospero, J.M., Swietlicki, E., Berg O. H., Hillamo, R., and Mäkelä, T.: Chemical mass closure and assessment of the origin of the submicron aerosol in the marine boundary layer and the free troposphere at Tenerife during ACE-2, Tellus B, 52, 141–168, 2000.

Rinaldi, M., Emblico, L., Decesari, S., Fuzzi, S., Facchini, M. C., and Librando, V.: Chemical Characterization and Source Apportionment of Size-Segregated Aerosol Collected at an Urban Site in Sicily, Water Air Soil Poll., 185, 311–321, 2007.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics – from air pollution to climate change, New York, Wiley Interscience, 1998.

Spiel, D. E.: The number and size of jet drops produced by air bubbles bursting on a fresh water surface, J. Geophys. Res., 99, 10289–10296, 1994.

Spiel, D. E.: A hypothesis concerning the peak in film drop production as function of bubble size, J. Geophys. Res., 102, 1153–1161, 1997.

Spiel, D. E.: On the births of film drops from bubbles bursting on seawater surfaces, J. Geophys. Res., 103, 24907–24918, 1998.

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 the physico-chemical properties of North Atlantic marine atmospheric aerosols, J. Geophys. Res., 112, D04206, doi:10.1029/2005JD007044, 2007.