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Coastal and open ocean aerosol characteristics: investigating the representativeness of coastal aerosol sampling over the North-East Atlantic Ocean

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Abstract

In order to achieve a better understanding of the modifications of the physical and chemical properties of marine aerosol particles during transport from offshore to the coast, size distribution and chemical composition were measured concurrently in clean air masses over the open North Atlantic Ocean and at an Irish coastal site. Open ocean sampling was performed on board the oceanographic vessel Celtic Explorer sailing 100–300 km off the Irish west coast, while coastal measurements were performed at the Mace Head GAW station. The experiment took place between 11 June and 6 July 2006, during the period of phytoplankton bloom.

The number size distribution and size-resolved chemical composition of coastal and open ocean samples were very similar, indicating homogeneous physical and chemical aerosol properties over a wide region in the marine boundary layer. The results also show that submicron chemical and physical aerosol properties measured at the coastal Mace Head Atmospheric Research Station were not unduly influenced by coastal artefacts and are thus representative of open water properties. Greater differences between the coastal site and the open ocean were observed for the aerosol supermicron sea spray components; this could be due to a variety of reasons, ranging from higher local wind speeds at the coastal site over the comparison period, to differences in sampling heights and increased local surf-zone production.

Evidence of ageing processes was observed: at the costal site the ratio between non-sea-salt sulphate and methanesulphonic acid was higher, and the aerosol water soluble organic compounds were more oxidized than in the open ocean.

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).

Until the 1990s, the open ocean was considered the most important source of sea spray aerosol. Subsequent studies investigated surf-zone effects in the production of aerosols by means of physical and optical measurements. Lidar studies undertaken in 1990 at Wallops Island, Virginia, showed a backscatter increase of two orders of magnitude over surf (Hooper and Martin, 1999). Additionally, the effects of the shore-line on coastal particle concentrations and size distributions were evidenced by lidar measurements at several stations on the Polish coast of the Baltic Sea (Zielinski, 1997, 2003a). Zielinski (2003b) also investigated the influence of sea bottom on coastal par-ticle production, concluding that the production of particles is more intense at coastal sites characterized by a gentle sea bottom slope.

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 $10\,\mu$m, 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.

Surf-zone particle production was also investigated at Mace Head, on the west coast of Ireland, during the PARFORCE campaign in 1998–1999, by means of lidar scans, revealing 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 surf-zone processes on the chemical composition of marine aerosol. 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 (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 surf-zone-generated aerosol might contribute between 5–20% of the aerosol particle mass concentration at Mace Head in the 3 to 30 m surface layer, but argued that the effect on chemical composition and subsequent chemical fluxes was not significant.

The aim of the present work is to achieve a better understanding of the extent to which the physical and chemical properties of marine aerosol produced over the open ocean are actually retained at the coast, and to assess the influence of the wave-breaking zone. To this end, a comparison was made among number size distributions and size-segregated chemical analyses of coastal and open ocean aerosol samples, collected in clean air masses in a period of high biological activity.

2 Experimental set up

The field experiment was carried out as part of the EU Project MAP (Marine Aerosol Production) (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 re-

search 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 search of highly biologically active sea waters, as monitored by satellite (MODIS).

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 cm^{-3}, and (c) having black carbon concentrations lower than 50 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.

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 0.01 to 0.50 μm. Aerosol was collected through the laminar flow community air sampling system, which has a stainless steel tube of 10 cm diameter 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) with a time resolution of 10 min. One of the DMPS operated in the 3–50 nm particles size range, the other in the 15–950 nm size range. During analysis, these data were combined to yield 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 char-

acterization 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). On the ship, both samplers were placed 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 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 stage of the impactors (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. Aliquots of the high volume samples were analyzed 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 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 $0.2\,\mu g$ of carbon and the accuracy of the TC measurement was better than 5% for $1\,\mu g$ 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., 2008). 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 each aerosol component concentrations are reported in Table 2.

3 Results and discussion

3.1 Aerosol number size-distribution

Figure 2 shows average aerosol number distributions measured at MH and onboard the CE; the whole period is divided into three sub-periods, according to the Berner impactor running time onboard CE. Only data collected within the clean sector (see Sect. 2),

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both at MH and onboard the CE, were used. The comparison cannot be performed for the period 21–25 June, as no measurements were performed on the ship. The size distributions reported in Fig. 2 present the typical features of remote marine aerosol populations, with two modes in the 0.01–1 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).

The number concentrations were very similar at MH and over the open ocean during period 1 (469 and 380 particles cm^{-3} for MH and CE, respectively). The higher average total number at MH was caused by coastal nucleation events. In fact, the MH size distribution was characterized by a higher average concentration of particles in the 10–20 nm size range. Both Aitken and accumulation mode particles were slightly shifted in size, especially the latter.

The spectra were different for period 2: the accumulation mode exhibited lower particle numbers and lower mean modal diameter over the open ocean. During this period, particularly on 18 and 19 June, meteorological charts show the passage of a low pressure system over Ireland, associated with variable wind directions in the area of the experiment. HYSPLIT back-trajectories for these days show an inflow of clean Arctic air toward the CE, and mid-Atlantic air masses toward MH. Therefore, the size distribution mismatch is in part due to different air masses, although both clean, at the two sites.

The spectra agreed closely during period 3, both in shape and particle number concentrations (542 and 530 particles cm^{-3}).

Physical aerosol spectra represented slightly different clean air masses due to a somewhat different geographical location of CE relative to Mace Head. It is therefore difficult to examine spectral differences closely, but an attempt was made to corroborate observed spectral differences by physical processes in the atmosphere. The most significant differences were observed in accumulation mode size and number. The

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accumulation mode size shifted from about 200 nm (CE) to 300 nm (MH). The accumulation mode number increased by between 40 and 90 particles cm^{-3} during periods 1 and 2, respectively. CE was up to 300 km further in open ocean relative to Mace Head, which translated into 10 h passage time (at 10 m s^{-1} wind speed), assuming a connecting flow. Primary aerosol production can be estimated from the accumulation mode particle fluxes measured by Geever et al. (2005), which resulted in an additional 20–40 particles cm^{-3} in the accumulation mode. The estimation did not, however, include deposition losses. The number of primary particles mainly explain the accumulation mode particle number increase during period 1. However, primary components (sea salt and WIOC) accounted for lower mass percentage (see next paragraph) than secondary components (nss-SO$_4^{-2}$ and WSOC). Therefore certain atmospheric processes must have also contributed to the observed spectral differences. Atmospheric processes were considered according to the approach of O'Dowd et al. (2000): condensation growth from gaseous precursors, like H$_2$SO$_4$ vapour, on existing aerosol, coagulation growth, cloud-free heterogeneous oxidation, in-cloud coalescence and in-cloud heterogeneous oxidation. The first three processes could not explain the observed growth of 100 nm due to either very low H$_2$SO$_4$ vapour concentration (<0.2 ppt; Aufmhoff et al., 2007) or very low aerosol number concentration (~400 particles cm^{-3}), since it would have required a time scale of several weeks for particles to grow to the observed sizes. In-cloud heterogeneous oxidation was the only mechanism capable of producing observed growth. Even at low SO$_2$ and H$_2$SO$_4$ concentrations the required time scale was 1–2 h, and certainly less than 10 h assuming connecting flow between CE and MH. Moreover, the most significant chemical component of the measured aerosol mass was nss-SO$_4^{-2}$, which is in accordance with in-cloud heterogeneous oxidation mechanism. WSOC also exhibited more oxidised features as will be discussed below.

3.2 Main chemical component concentrations

Figure 3 shows a comparison of the size segregated aerosol chemical components at MH and over the open ocean, while Table 3 reports the average fine and coarse concentrations. The concentrations at MH and onboard the CE exhibit similar features for many compounds. However, some exceptions were observed, regarding sea salt (coarse fraction), WIOC and MSA, which will be analyzed in greater detail below.

Non-sea-salt sulphate (nss-SO_4^{-2}) (Fig. 3a and 3b) 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 evident in samples MH2, MH3 and CE2.

Ammonium (NH_4^+) was detected in comparable concentration and mass size distribution at MH and over the open ocean. Submicron NH_4^+ concentration was always below the remote marine background concentrations reported by Jickells et al. (2003). Nitrate (NO_3^-) was detected in all samples in the coarse mode, as a result of the reaction of gaseous nitric acid with NaCl. Indeed, both data sets show Cl/Na ratios lower than the seawater ratio of 1.8 (Seinfeld and Pandis, 1998).

Similarities between the two data sets in the case of WSOC mass-size distribution can be observed (Fig. 3c and 3d). The WSOC exhibits a bimodal distribution, with a submicron and a supermicron mode. The average mass size-distributions for WSOC measured at MH is not substantially different from those determined over the open ocean, although for specific pairs of samples the size distributions do not show a perfect match (for example, MH3 vs. CE3).

Sea salt concentrations (Fig. 3e and 3f) differ significantly between MH and CE, with higher sea salt average concentrations at MH (140% with respect to CE) in the 1.0–8.0 μm size range. Moreover, the sea salt mass size distribution is highly variable at MH, the three samples each exhibiting different size distributions, while all the open ocean samples are characterised by a peak in the distribution in the 2.0–4.0 μm size range. Fine sea salt reveals a different behaviour, having similar concentrations in CE

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and MH samples (difference of 5%, within the random uncertainty range).

The WIOC atmospheric concentrations, measured on the high volume filters (Fig. 4), show significant differences between the two datasets: average fine WIOC concentration at MH is 62% of that measured over the open ocean, while in the coarse fraction, the average concentration at the coastal site is 182% the one onboard the CE. Over the open ocean, the concentration of WIOC in the fine mode is 2.7 ($\pm$1.4) times that of the coarse mode, while in the coastal samples the ratio between the two modes is 0.9 ($\pm$0.3). Clearly, WIOC behaved differently at the two sampling sites, with more intense sources for the submicron fraction over the open ocean, and more efficient ones for the super-micron fraction at the coastal site.

Figure 5 reports the size-segregated chemical composition of the aerosol samples collected at MH and onboard the CE averaged over the whole campaign. In each size interval, the mass contribution of each species is normalized to the sum of all the analyzed species. The size-resolved mass fractions for water insoluble organics were extrapolated from the high volume data, using the same procedure of Cavalli et al. (2004).

At both sites, the main components of the fine aerosol fraction are nss-SO_4^{-2} and WSOM (WSOM=WSOC$\times$1.8). The former accounts for 44$\pm$6 and 45$\pm$1% of the fine aerosol mass at the coastal site and open ocean, respectively, while the latter contributes 27$\pm$6 and 26$\pm$2% at MH and on the CE, respectively. In contrast with observations during previous campaigns at MH (Cavalli et al., 2004; O'Dowd et al., 2004), water insoluble organic matter (WIOM=WIOC$\times$1.4) accounts for only 8$\pm$0.1 and 12$\pm$3% 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$\pm$5% and 90$\pm$2% of the submicron mass at MH and onboard CE, respectively). Figure 5 shows that, despite the differences between the MH and CE samples in the WIOC contribution and absolute concentrations of coarse mode sea salt and WIOC, the average size-segregated chemical composition is very much the same at the two sites during the observation period. These results are the first

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direct observations that coastal effects influencing the aerosol chemical composition in marine air masses at MH are small.

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 processes 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 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 case 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., 2008). The higher coastal super-micron sea salt and WIOC concentrations presented in Figs. 3 and 4 suggest that surf-zone wave breaking can enhance the production of coarse particles consisting of internally mixed sea salt and insoluble organics. These findings are in agreement with the results of de Leeuw et al. (2000), who showed a size-dependent coastal effect. Nevertheless, other contributing factors must also be considered: average wind speed over the sampling period at the coastal site was 1.8 (±0.4) times that measured over the open ocean, potentially enhancing the production of large spray particles. Moreover, the different sampling height (14 m above the ship deck and 10 m at MH) might have affected, at least partially, the measurements of sea salt concentration in the largest size range (4.0–8.0 μm), where a steep vertical gradient is often observed in the marine boundary layer.

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

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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 Organic composition

Methanesulfonic acid (MSA) was the main organic compound detected in the impactor and filter samples collected during MAP. Figure 3g and 3h report the MSA size distribution for coastal and open ocean samples, highlighting many differences between the two locations. MH samples exhibit comparable MSA concentrations in the fine and coarse mode, samples MH1 and MH3 making the greatest MSA contribution in the 1.0–2.0 μm size range. Conversely, the open ocean MSA size distribution peaks in the accumulation mode (0.25–0.5 μm), with higher concentrations than the MH samples in the 0.25–1.0 μm size range.

The average nss-SO_4^{-2}/MSA ratio is 3.56±0.76 for submicron particles at MH and 2.68±0.32 onboard the CE. This difference can be attributed to the oxidation of MSA to nss-SO_4^{-2} in the marine boundary layer during transport. The presence of more oxidized sulphur species can be interpreted as evidence of more aged coastal particles than those collected over the ocean. The difference is less pronounced in the coarse size range, probably due to the 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 6 shows the functional group distributions for coastal and open ocean samples. The sample sets exhibit very similar water soluble organic functional group distributions, with a larger contribution from the purely alkylic

groups (H-C), aliphatic groups adjacent to unsaturated carbon atoms (H-C-C=) and methyl groups of MSA. Interestingly, the same evolution of the functional group composition was observed during the experiment in the two datasets: during the first part of the experiment, when samples MH1 and CE1 were collected, the maximum contribu-
5 tion of the MSA signal was observed at both sampling locations. The rest of the signal was mainly associated to aliphatic structures and to H-C-C= functional groups, which, given the scarce aromatic/alkene content of the samples, can be associated entirely to oxidized moieties (H-C-C=O groups, either ketones or carboxylic groups). During the last part of the campaign, in samples CE3 and MH3, the functional group composition
10 exhibited similar changes to those observed in previous samples: the MSA contribution was at a minimum, while the signal from H-C-O groups (deriving from polyols, possibly including carbohydrates) increased its contribution to a maximum. In the intermediate period (CE2 and MH2) functional group composition showed mixed features of those observed during the first and third parts of the campaign.
15 Alongside these common features of the NMR spectra between MH and CE, some systematic differences were also found. The contribution of nitrogen bearing aliphatic groups (H-C-N) ranged between 2 and 3% at MH and between 5 and 7% over the open ocean. The main difference between the two sets of data is the higher contribution of purely alkylic groups (C-H) onboard the CE. The calculated ratios between
20 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 of MSA and inorganic ion concentrations, the latter finding, suggests that aerosol particles undergo oxidation during the advection to the Irish coast.

4   Conclusions

25 Clean marine aerosol number size distribution and relative chemical composition were very similar at the coastal and open ocean locations, indicating homogeneous physical and chemical aerosol properties over a wide region in the MBL. The results imply that

marine aerosol chemical composition is determined by large scale processes such as phytoplankton activity, whitecap formation, photochemical activity and synoptic meteorology.

In addition, it is found that the wave-breaking zone does not significantly influence marine aerosol properties in the submicron size range. Only coarse sea salt and WIOC concentrations (but not their relative contribution to sea spray) exhibited substantial differences between the coastal site and the open ocean, attributable to the surf-zone effect.

The slightly higher contribution of WIOM to total submicron mass, measured over the ocean further demonstrates that the presence of primary organics in fine marine aerosol is not related to small scale coastal effects but to a source spread over the oceanic surface. This finding confirms the conclusions of Ceburnis et al. (2008), who estimated that the absolute concentration footprint of primary aerosol species is of the order of a hundred kilometres in the open ocean, while the contribution of coastal or surf-zone emissions is not significant.

Such evidence suggests that coastal aerosol measurements are representative of remote oceanic conditions, providing that local sources are excluded by selective sampling in clean air masses.

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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	12/06/06	19/06/06	80.3
CE1	12/06/06	15/06/06	64.0
MH2	19/06/06	28/06/06	50.0
CE2	16/06/06	20/06/06	57.2
MH3	28/06/06	05/07/06	36.0
CE3	26/06/06	04/07/06	59.7

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

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Table 3. Average atmospheric concentration (μg m^{-3}) of the main aerosol components; standard deviation of the mean value are 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	
	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)
NO$_3^-$	0.002 (0.003)	0.001 (0.002)	0.18 (0.09)	0.13 (0.09)
sea salt	0.07 (0.02)	0.07 (0.04)	4.21 (0.54)	3.00 (0.81)
WSOC	0.13 (0.03)	0.14 (0.05)	0.09 (0.06)	0.07 (0.02)
WIOC	0.05 (0.01)	0.08 (0.01)	0.07 (0.03)	0.04 (0.02)
MSA	0.11 (0.02)	0.17 (0.06)	0.09 (0.03)	0.08 (0.03)

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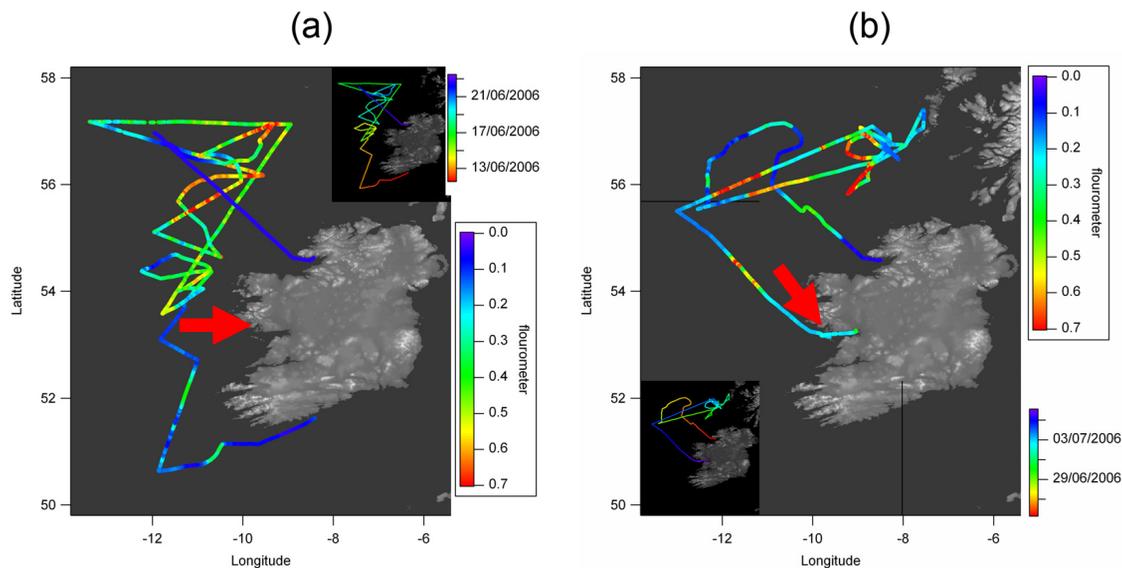
Fig. 1. The Celtic Explorer cruise route (**a**: from 11 to 22 June, **b**: from 25 June to 5 July); the colour of the route in the two large images represents the chlorophyll-*a* signal from the ship fluorometer (in the smaller inserted images they refer to the date, see the appropriate scale). The red arrows indicate the location of the Mace Head Research Station.
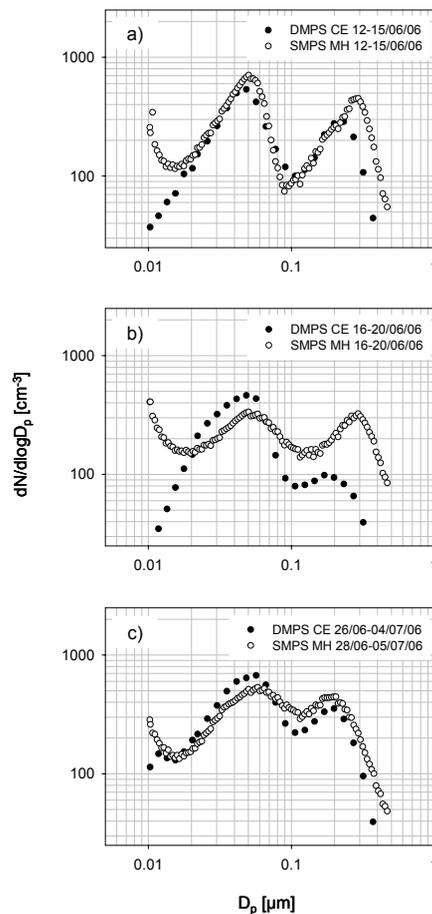
Fig. 2. Aerosol number size distributions measured at Mace Head (MH) and over the open ocean (CE): **(a)** average from 12 to 15 June, **(b)** average from 16 to 20 June, **(c)** average from 26 June to 5 July.
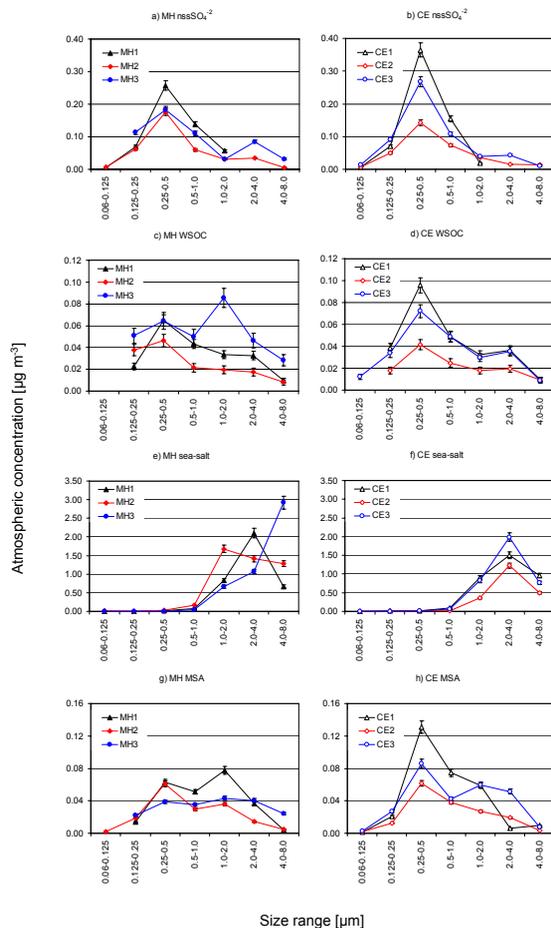
Fig. 3. Mass size distribution of the main aerosol components measured at Mace Head (MH) and onboard the Celtic Explorer (CE). Error bars refer to the experimental random uncertainty (see Sect. 2).

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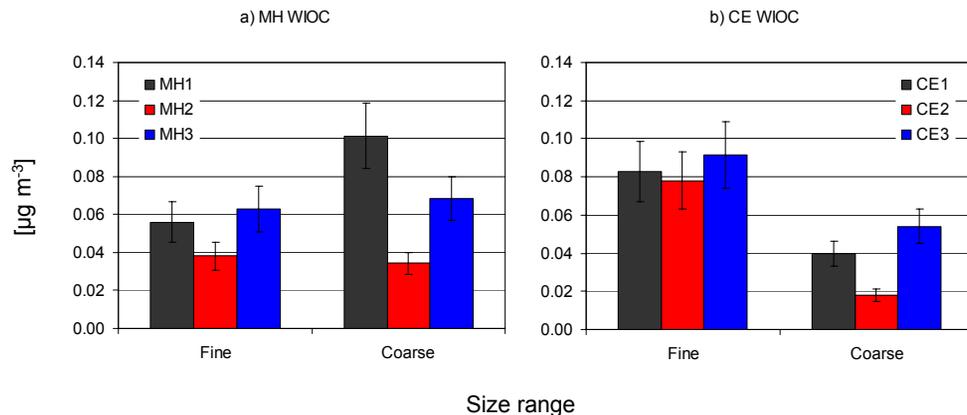
Fig. 4. Aerosol WIOC concentration in fine ($D_p < 1.5\,\mu$m) and coarse ($D_p > 1.5\mu$m) size ranges measured **(a)** at Mace Head (MH) and **(b)** onboard the Celtic Explorer (CE). Error bars refer to the experimental random uncertainty (see Sect. 2).
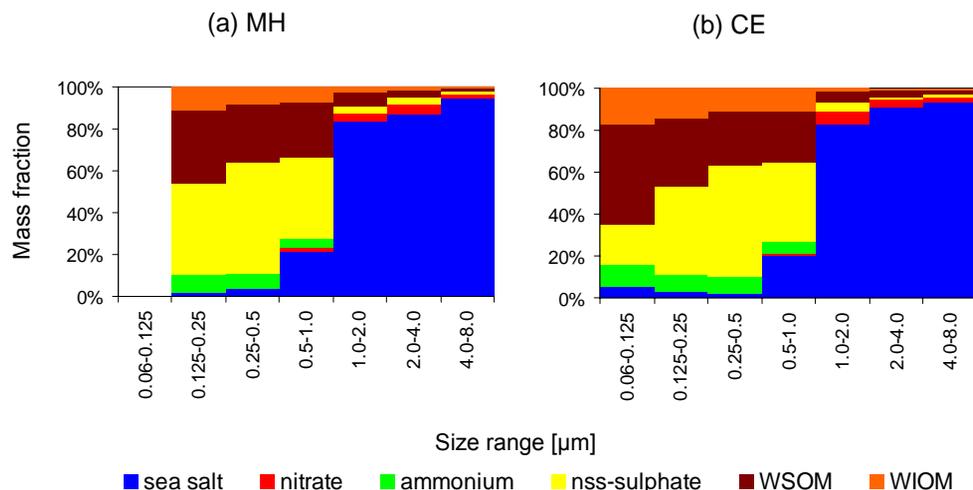
Fig. 5. Average relative chemical composition of coastal (MH) and open ocean (CE) aerosols. The aerosol chemical composition in the size range 0.06–0.125 μm is not shown for MH, since the concentration of organics was below detection limit for all three samples (the detection limit for organics is about one order of magnitude higher than that of inorganic ions due to different instrumental sensitivity and different field blank values).
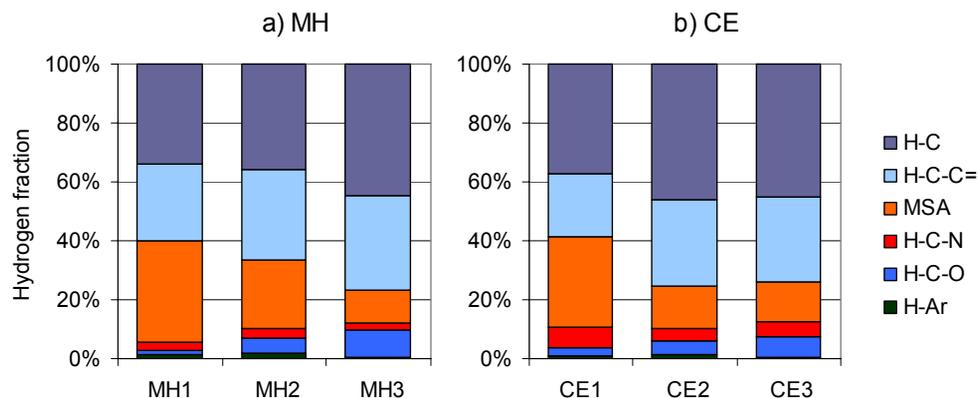
Fig. 6. Functional group relative composition of WSOC in Mace Head **(a)** and Celtic Explorer **(b)** samples. H-Ar, aromatic protons; H-C-O, protons bound to oxygenated aliphatic carbon atoms; H-C-N, protons bound to aliphatic carbon atoms bearing nitrogen atoms; MSA, methansulphonate; H-C-C=, protons bound to aliphatic carbon atoms adjacent to unsaturated groups; H-C, purely alkylic protons.