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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Coastal and open ocean aerosol characteristics: investigating the representativeness of coastal aerosol sampling over the North-East Atlantic Ocean" *by* M. Rinaldi et al.

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On reflection, we have used confusing terminology which introduces confusion in terms of the objectives of the paper and we thank the reviewer for clearly pointing this out, along with providing useful suggestions for improvement. In summary, it was not our intention to show that marine aerosol over the NE Atlantic is homogeneous in nature (in terms of all properties) as this would clearly promote a concept of no evolution in aerosol properties. It was our intention to demonstrate that measurements of aerosol properties, if conducted in the correct manner, at Mace Head were representative of marine aerosol properties at that location and free from notable coastal sources and

influences. In this context, we have reformulated the title (Aerosol sampling at Mace Head: is there evidence for local coastal influences compared to off-shore measurements?) and added content, in particular a more objective analysis of similarities and differences, as requested by the reviewers. In summary, we demonstrate that while there are differences in some aerosol properties at Mace Head and off-shore on the research vessel, only differences associated with the nucleation mode can be attributed to coastal sources. More so, and perhaps the real essence of the paper, is that we show that the "chemical fingerprint" - that is the size segregated fractional contribution of dominant chemical species is, to all intents and purposes, practically identical for Mace Head samples and off-shore samples. The main point here is that the observed organic enrichment previously reported at Mace Head is not as a result of a coastal source of organics. We acknowledge that our data refer to a specific time period of year 2006 and cannot account for the seasonal and interannual variability and that their validity is limited to Mace Head or very similar coastal sites. On the other hand, this was the first experiment allowing simultaneous aerosol measurements at a coastal European site and off-shore in the Atlantic Ocean, and our results support that the aerosol properties measured at a height of 10 m at Mace Head are representative of NE Atlantic marine aerosol encountered at 54N and 9W. Below, are reported the answers to each of the referee's comments.

[Referee 2] The authors present three aerosol number distribution plots (Fig. 2) as one piece of evidence to show that the MH and open ocean sites are similar, but are they really? The basis for this "similarity" in the manuscript is subjective. What is needed is a quantitative assessment with set criteria to evaluate the degree of similarity or difference in these three data sets. Even when viewed on a log scale, I would argue that the distributions between the two sites are more different than similar. From the number distribution data, there are two data sets that somewhat agree and one that clearly does not (panel b in Figure 2). This is not sufficient to make a broad sweeping statement about homogeneity.

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[Response] Physical measurements were used in the paper to support the conclusions obtained with chemical measurements, even though, for obvious size and time resolution differences, physical and chemical measurements can hardly be compared. Similarities between the size distributions are undeniable, but we admit that the comparison has been done only qualitatively and not capitalizing the high time resolution of the physical measurements. According to the referee's comments, a new approach to the size distribution comparison has been developed and it will be proposed in the revised manuscript. The campaign period has been divided into four sub-periods characterized by homogeneous air mass origin and good trajectory agreement (based on HYSPLIT back-trajectories). Number size distributions have been quantitatively compared in terms of particle number in three size ranges: nucleation ($<$20nm), Aitken (20-80 nm) and accumulation (80-300nm) mode. It resulted that:

- The nucleation mode clearly exhibited elevated concentrations at Mace Head compared to off-shore concentrations and point 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 MH and the CE: average absolute difference in particle number was 20% ranging from -37% to +12%.

- Accumulation mode concentrations showed averagely 35% higher concentrations at Mace Head.

Considering that the standard deviations associated to the mean particle number at both sites are of the same magnitude (often higher) than the differences evidenced between the two datasets, these differences are not enough to conclude a significant effect of the shoreline on physical coastal measurements.

[Referee 2] Related to this issue, even though sampling was sectored, what were the synoptic air trajectories during sampling?

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[Response] Given the sampling strategy adopted for the impactors, the samples have been collected only in air masses coming from the Atlantic Ocean. Air mass back-trajectories have been calculated, by HYSPLIT, in parallel for MH and the CE, with a time resolution of 12 h. It resulted that the backtrajectories with endpoints in MH and CE typically originated in the same area of the Atlantic Ocean, with 73% of the pairs of trajectories looking as streamlines of the same regional flow intercepting both MH and CE. Usually, the two sampling sites were interested by parallel streamlines spaced by 50 - 100 km. Most of the backtrajectories highlighted the main atmospheric circulation patterns encountered during the campaign, which can be classified into: (a) N. Atlantic cyclonic air masses together with Greenland and Arctic air masses and (b) mid Atlantic air masses (coming from West and South-West). The back-trajectory analysis support our approach: the two sampling sites were interested for the major part of the time by air masses that have travelled over the same areas of the Ocean and that have been influenced by the same processes and sources, so that similar aerosol characteristics can be assumed. Therefore, if a systematic bias is introduced in the aerosol chemical composition because of the shoreline proximity at MH, it should be evident in the average aerosol chemical composition. A new paragraph dealing with the back-trajectory analysis will be added in revised version of the manuscript.

[Referee 2] In order to conclude large scale homogeneity in the MBL (I'm assuming that they're talking about the NE Atlantic, but as stated in the abstract and conclusion this is poorly worded), it is important to have a much larger sampling grid with more stations and seasons covered.

[Response] As stated above, to demonstrate large scale homogeneity in the MBL was not the purpose of the paper, even though we have referred to this in the conclusions. The number of chemical samples may appear limited, given that each sample requires approximately one week of sampling time but, as we are sure you are well aware, this is the nature of marine aerosol chemistry sampling and the number should not influence the importance of each sample. Clearly, given shiptime costs, it is prohibitive to have

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a ship upwind of Mace Head for an extended time compared to the month-long cruise reported here.

[Referee 2] Additionally, although the authors performed sectored sampling and used the criteria that aerosol numbers needed to be low, what does this really tell us about MH versus the open ocean site-that they are "similar" under a restricted set of conditions at a very specific time of year? The air that they've sampled is certainly not purely marine, and local/regional influences at MH are well known (see comment 3).

[Response] 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 condition. Even though we cannot exclude some degree of contamination in MH samples, 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.

[Referee 2] With respect to the chemical size distribution data, it would be useful to see ammonia and nitrate concentration and mass size distribution comparisons since they were reported to be similar between the two sites. Is the WSOC measured at MH really not substantially different from that at CE even though size distributions do not show a perfect match (pg 7, bottom)? From my perspective, I do not see particularly good agreement for any given sampling date. Again, a quantitative assessment would be useful.

[Response] Size distributions for every sample were reported to show the size distribution and concentration variability within each dataset. Samples cannot be compared in couples (MH1 vs CE1, MH2 vs CE2, etc...) because of the not matching sampling periods. The quantitative assessment have been done only on the monthly average concentrations, obtained averaging the three time-integrated samples collected at the two sites, and all the conclusions reported in the paper derive from this assessment. A statistical significance test has been applied to the size resolved and fine/coarse av-

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erage data: no significant differences between the two datasets have been highlighted at a confidence level of 0.05. Given the small number of samples and the variability of concentration and mass size distributions between samples, only differences of the order of a factor of 2 between the average concentrations at MH and onboard the CE can be considered significant. Differences of this magnitude are not present between the two average data sets. The highest "t" values, suggesting the lowest degree of similarity, resulted associated to WIOC, coarse sea salt and fine MSA, as discussed in the text. Although the observed differences between the average concentrations of the chemical compounds are not significant in statistical terms, the possible effects of coastal processes can be investigated by comparing the anomaly in the concentration of a given chemical constituent with the anomaly of a species whose formation processes are known. Following this approach, the behaviour of nssSO4 and NH4+ can be used as a reference. In fact, nssSO4 and NH4+ in the marine boundary layer are produced by secondary sources spread over the ocean and there is no evidence that coastal processes, in particular the spray production at the wave-breaking zone, can enhance their atmospheric concentrations. The ratio between CE and MH average concentrations of nssSO4 and NH4+ ranges between 0.5 and 1.5 depending on the size interval. Therefore, ratios within this range for any aerosol component have to be considered as due to differences in air mass characteristics or to sampling and analysis uncertainty, 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. Following this approach, no "significant"; coastal influence on the aerosol chemical composition is evident: only sea salt and nitrate in the size range 4.0-8.0 μm present a CE/MH ratio lower than 0.5 (0.45). A "significant" difference can also be observed in the 0.06-0.125 μm stage of the impactor (0.3) for sea salt, but this difference can be attributed to the very high uncertainty in chemical analyses due to concentrations close to the detection limit. By contrast, the fine CE/MH ratio of WIOC resulted 1.6, suggesting some significant difference, but pointing to a stronger source of insoluble organics over the open ocean. Finally, size distributions of ammonium and nitrate were not reported in the

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text because they represent only a minor portion of the aerosol mass and were undetectable in many stages; they will be showed in the revised version of the manuscript.

[Referee 2] The authors state "Figure 5 shows that, in spite of the differences between the MH and CE samples regarding the contribution of WIOC and the 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 direct observations that coastal effects influencing the aerosol chemical composition in marine air masses at MH are small." When I examine Fig. 5, I don’t see that the data are "very much the same" and therefore I am not convinced that there are not local/regional emissions affecting aerosol properties measured at MH.

[Response] The average contributions of the chemical compounds to aerosol mass in the different size intervals, reported in Figure 5, presented differences of less than 5% at MH and on board the CE. This means that the "chemical fingerprint" is, to all intents and purposes, practically identical for Mace Head samples and off-shore samples.

[Referee 2] Indeed, the literature has clearly demonstrated such influences. For example, continental air containing reaction products from emissions over Europe is episodically recirculated and entrained into the MBL over eastern North Atlantic and sampled during on-shore flow at Mace Head (e.g., Savoie et al. 2002. JGR). Given the prevailing westerly flow at this location, presumably, on average, such continental influences would diminish with distance unwind from the coast yielding a gradient rather than a "homogeneous" distribution of aerosol properties over the region.

[Response] As already discussed above, to demonstrate homogeneous distribution of aerosol properties over the East North Atlantic was not the aim of the paper, the expression was used in the text in a misleading way and this point will be modified and cleared in the revised version of the manuscript. What our data show is that during the campaign, in periods during which the anthropic influence at MH was low, no significant

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difference has been observed in the chemical composition of coastal and open ocean aerosol samples and only minor differences have been observed in particle number, in Aitken and accumulation mode. We do not exclude that under different conditions (i.e. under more intense continental outflow) this can be not true.

[Referee 2] In addition, emissions of IO precursors from coastal macroalgae have been linked to bursts of new particle production at Mace Head (e.g., O’Dowd et al. 1999, GRL; O’Dowd et al. 2002. Nature). Presumably this local source would influence aerosol physical properties measured at Mace Head on occasion (e.g., under conditions of in-sector flow roughly parallel to the coast or in-sector flow over the off-shore islands). Certainly, selection of periods during which aerosol number concentrations are low would tend to minimize the influences of local/ regional emissions from the perspective of the authors’ analysis. However, this filtering does not eliminate the influences of these processes on aerosol properties in the region. What is the rationale in focusing an analysis such as this exclusively on the lower end of the distribution in aerosol number concentrations? If the goal is to evaluate the regional representativeness of aerosol properties measured at MH, it would seem more appropriate to interpret the full range of conditions rather than a selected subset thereof.

[Response] As explained in the paper we believe that newly formed particles cannot influence the aerosol chemical composition measured with the adopted size resolution. As for the size distribution the effect of new particle formation bursts is evident at MH, but a full discussion on new particle formation near the coast and over the open ocean is not among the purposes of this manuscript. As for the fact that we focused "exclusively on the lower end of the distribution in aerosol number concentration" it is due to the necessity of excluding local anthropogenic sources: the goal of our work is to evaluate if the "clean sector" sampling at MH is representative of open ocean condition, not if any sample collected at MH is representative of open ocean condition.

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