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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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We accept the Referee's criticisms concerning the non rigorous presentation of the experimental data. Admittedly, in the original version of the manuscript we have used rather subjective definitions of similarity, while more quantitative ways of expressing the anomalies are certainly required and can be easily implemented in the revised version of the paper. This lack of rigor in the data presentation may have led to a general scepticism of the Referee about the significance of the experimental results. However, none of the Referee's objections can really invalidate the main findings of the field experiment:

- During the observation period, the difference (anomaly) in the size-segregated mass concentrations of all the major organic and inorganic chemical compounds between the MH station and the CE platform is of the same order of magnitude of that observed for species (like nss-SO4 and NH4) not having a coastal source, with very few exceptions like seasalt in very large particles;

- The average contributions of the chemical compounds to aerosol mass in the different size intervals were the same (with less than 5% of difference) at MH and on board the CE;

- The comparison of time-integrated number size distributions shows that only the nucleation mode was strongly affected by coastal formation processes.

We conclude therefore, that during the experiment no evidence was found for local coastal influence at MH in respect to the size distribution and chemical composition of aerosol particles having diameters between 20 nm and 4 μm. We acknowledge that our data refer to a specific time period of year 2006 and cannot account for the seasonal and interannual variability. 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.

[Referee 1] The manuscript lacks scientific rigor. The hypotheses are not well stated or tested. Neither are the goals or objective explicitly stated.

[Response] In the paper, 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

ACPD

8, S10929–S10935, 2009

and differences, as requested by the reviewer. 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. The hypotheses have been tested based on the available experimental data, and our conclusions hold for the conditions explored in this study, which are representative for the warm season in Mace Head, and do not necessarily apply to other seasons. Such limitations can be stated more explicitly in the paper in order to avoid that our results are extrapolated to conditions not investigated in this study.

[Referee 1] The differences between the open ocean and coastal measurements are not quantified in terms of a quantitative difference (anomaly) and statistical significance of that difference.

[Response] Given the difficulties in coordinating the automated clean marine sector sampling at Mace Head with the offshore sampling, aerosol samples have not been collected with 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 values for the campaign, obtained as the average of the three time-integrated samples collected at each sampling site. In the revised version of the paper we will provide the size-segregated average atmospheric concentration (with standard deviation bars) for each aerosol component, together with (or instead of) single-sample size distributions. A statistical significance test has been applied to the size resolved and fine/coarse average 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 would be considered significant. Differences of this magnitude are not present between the two average data sets for any compounds. The highest "t" val-

ACPD

8, S10929–S10935, 2009

ues, suggesting the lowest degree of similarity, results associated to WIOC, coarse sea salt and fine MSA, as already pointed out in the manuscript. 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, 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. 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. As for physical measurements, 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. The result is 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.

ACPD

8, S10929–S10935, 2009

- 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 1] The conclusions do not show progress over the results discussed in the literature summary in the introduction.

[Response] We do not agree with this statement of Referee #1. To our knowledge this is the first paper presenting aerosol chemical composition data collected by parallel measurements at a clean European coastal site and over the open Atlantic Ocean. The results have important implications for the representativeness of coastal sampling in describing open ocean aerosol chemical composition.

[Referee 1] Without more information about the height of the sampling inlets compared to the surf plumes near the coast or the breaking wave plumes on the open ocean, and the trajectory connection between the ship and land station, it is difficult to tell what the data represent and whether a difference is to be expected at all.

[Response] Information about the plumes height are not available and cannot be derived from the available measurements. Nevertheless, we have provided all relevant information on sampling heights: sampling heights both at MH and onboard the CE are made at least at the recommended sampling height at greater or equal that 10 m. Part of plumes can mix to any height and our sampling set up is no different from any previous ship based sampling programme. Given the sampling strategy adopted for the

ACPD

8, S10929–S10935, 2009

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 1] The ship's location was dictated by "highly biologically active sea waters, as monitored by satellite". Did this affect the representativeness of the sampling in any other way?

[Response] We do not think that the location of the ship over highly biologically active sea water can influence the representativeness of the open ocean sampling. Aerosol chemical characteristics are not directly dependant on the biologic activity going on in the sea water directly below the sampling point, but, given the size of the particles and their residence time in the atmosphere, it can result from processes taking place in a rather vast area surrounding the sampling point. The choice of locating the ship over the most highly biologically active waters in the North Atlantic was dictated by the ne-

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8, S10929–S10935, 2009

cessity of conducting laboratory experiments on board the ship that are not discussed in this paper.

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