

Interactive comment on “Marine submicron aerosol sources, sinks and chemical fluxes” by D. Ceburnis et al.

Anonymous Referee #4

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*** General comments**

This paper uses eddy covariance and chemical gradient measurements to explore aerosol fluxes from North Atlantic coastal waters off Mace Head, Ireland. It builds on an earlier study by the same authors (Ceburnis et al. GRL 2008). It is claimed that the present study improves on the earlier work because collocated eddy covariance measurements have now been added to the analysis, the sampling period is longer and covers a full year, and a wider range of chemical species have been measured with the gradient system. In fact, the new eddy covariance measurements are very similar to those used in the previous study, the year-long sampling period is not really exploited to observe seasonal trends, and the results drawn from the new chemical species are uncertain and conflicting. Therefore, this paper is not a major step forward from the

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earlier 2008 study. In addition, the paper is not very clearly written. The language and terminology is very loose at times and many strong statements are presented without sufficient argument with reference to the data or appropriate references. I detail specific instances below. Nevertheless, the new measurements are potentially useful and I find the comparison of the derived sea spray flux parameterisation with existing parameterisations interesting and instructive. Following extensive revisions I believe the paper is suitable for publication in ACP.

Given the substantial uncertainties involved in the measurements and their averaging, the paper would benefit from a more in-depth discussion of the physical processes responsible for establishing the concentration profiles. Such discussion was necessarily missing from the original, pilot paper since it was only a short letter published in GRL. The discussion is necessary because the profiles are used as a basis for quantifying fluxes as a function of wind speed (e.g. WIOM and WSOM), and it is important to know what these fluxes represent. The sea spray profile is well explained but there are issues concerning the secondary aerosol species that should be addressed more thoroughly: 1) The negative nitrate and oxalate profiles are a very surprising and interesting result and as such require further analysis. The authors suggest that the profiles show that these species had condensed onto pre-existing, primary sea salt particles, which also displayed a negative concentration profile. Support for this argument is provided in Fig. 6, at least for nitrate. But it is also calculated that the negative sea spray concentration profile arises due to sea spray emissions only 1–10 km (or 0.2–5 km, different values for the range given in different parts of the manuscript) from the measurement point (the flux footprint region). Was there enough time for acid-displacement reactions to enhance nitrate and oxalate concentrations in the sea spray particles as they were carried in onshore airflow to the coast? (To the extent that such distinct negative nitrate and oxalate profiles could be established). This question should be dealt with to establish confidence in the interpretation of the concentration profiles and calculation of the extent of the flux footprint region. 2) How were the positive concentration gradients established, and why do some secondary species display positive gradients

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while others have flat profiles? There is mention of deposition, lack of production and mixing throughout the paper with reference to individual profiles. But nowhere in this text or in the earlier GRL paper can I find a clear and unified discussion of the physical processes responsible for establishing concentration gradients for secondary species. Given these were PM1 particles, how important is deposition?

I take issue with the use of the curved lines used to represent the concentration profiles (e.g. Figs. 3 and 4). The issue is not just an aesthetic one. I assume the lines connecting points are to guide the eye and are not the functions fit to the data to calculate concentration gradients. They are confounding and potentially misleading because they suggest functional forms that haven't been shown to have any physical basis. It is especially confusing when multiple profiles are plotted on the same axis and when the profiles contain strong curves. I suggest that simple straight lines connecting points would be a better way to represent the data.

There are considerable uncertainties in the flux-wind speed relationships, as stated numerous times throughout the manuscript text (e.g. P23863, L10; P23864, L16; P23864, L22). This uncertainty needs to be reflected in the reported flux-wind speed relationships. For example, by reporting the 95% confidence intervals of all of the fitting parameters.

* Specific comments

P23848, L2: First sentence of the abstract says the objective of this study was "... to quantify seasonality" in aerosol fluxes. Seasonally resolved fluxes are not analysed or presented so this objective has not been achieved and this sentence should be changed accordingly.

P23852, L23: Provide references for the OM/OC factors and Na to SSS conversion factor

P23853, L6: The reasons for presenting normalised concentrations are clear and well

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explained. However, the measured absolute concentrations should also be presented somewhere to give readers a sense of what was actually measured and the uncertainties involved.

P23853, L8: How did the variances of the different profiles around the mean normalised concentrations compare to measurement uncertainties? Do the horizontal error bars in Fig. 3 represent the variances or uncertainties? Why was that decision made?

P23853, L24: Fluxes as a function of oceanic biological activity are not presented so this part of the sentence should be removed.

P23854, L4: Stull (1988) is not listed in the References section.

P23854, L20: How does this demonstrate that the K_z were normally distributed? Also, the averaged K_z values must be consistent with the high time resolution measurements, since they are averages of those measurements. I think the more relevant point from the comparison shown in Fig. 1 is the variance in K_z around the mean values, which is indicated by the high time resolution measurements, since this variance contributes to the uncertainty in fluxes calculated by Eq. (1).

P23855, L5: Fig 2 appears to represent only a subset of the data, which should be mentioned here.

P23855, L17: Norton et al., (2006) concluded that the height of the internal boundary layer is between 10 and 15 m.

P23856, Eq. (2): It is great that a whole section is devoted to errors and uncertainties but this is a very general equation. The equation should be presented in the form that it was applied in this study, including consistent notation (i.e. q changed to F). Specifically, what terms were included in the equation? What values were assigned to the individual uncertainties?

P23856, L6: The equation for OM_{ss} represents the mass fraction of OM in the sea spray, not the organic enrichment factor. Enrichment factor is the ratio of OM fractions

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in 2 different media (e.g. EF = OM_{ss} in aerosol/OM_{ss} in seawater) and represents the degree of organic enrichment in one medium relative to the other.

P23856, Eq. (3): It should be stated that this equation assumes WIOM represents total sea spray OM. Secondly, I've tried but can not derive this equation from the information presented here. Please check and confirm if the equation is correct.

p23856, L11: As per the comment above, this is the sea salt mass fraction in SSA, not the sea salt 'impoverishment' factor. Still, this number will always be less than 1.

P23857, L10: Typo. Should be "may have had..."?

P23857, L25: Are the differences really statistically significant? By eye, the differences in the concentration gradients from 3 to 10 m seem to be comparable to the differences in the gradients between 10 and 30 m. Broader point, going back to the general comment above its hard to judge these things from the curved lines currently linking the markers in Fig 3.

P23858, L5: This argument is difficult to follow. If the nitrate and oxalate are tied to the sea salt, why is sea salt profile also not 'distorted' by the deposition of large sea salt particles close to the ground? Also, the WIOM_production profile in the bottom right corner of Fig. 3 looks similar to the oxalate and nitrate profiles. How does that fit in with this discussion?

P23858, L23: The sentence beginning "Thus..." is very convoluted and needs to be broken up into smaller sentences.

P23858, L15: How many individual WIOM profiles were averaged to produce the average profile for each category? Since the dates when different profile types were observed is discussed it would also be good to indicate the category of each measured profile in Table 1, for example.

P23858, L15-29: This discussion is very speculative and needs to be flagged as such. And how does the wind speed fit into this picture? When these profiles are converted

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to fluxes later (P23863) a relationship with wind speed is discovered and discussed extensively. This discussion about biological activity neglects the influence of wind speed entirely.

P23859, L20: If so, this ambiguity should be reflected in the errors bars in Fig. 3.

P23859, L25: Fig. 5 does not seem to be explained or introduced anywhere. What is calculated NH4?

P23860, L2: Please explain more how the neutralisation profile could be an "...indication of the importance of in-cloud processes of sulphuric acid neutralisation."

P23860, L6: Related to the issue of the timescales of nitrate and oxalate uptake to sea salt particles, was there enough time for MSA uptake to sea salt particles to make this the "likely" explanation for the negative concentration gradient between 10 and 30 m, especially considering that there was a positive concentration gradient between 3 and 10 m.

P23860, L15: What was the criterion that was used to remove 8 of the 15 WSON profiles from the analysis?

P23861, L1: Useful to provide references for the secondary formation of these species.

P23861, L3: Given that the gradient method has produced results that conflict with existing knowledge of the secondary nature of these aerosol species, how can the method be used as a basis for quantifying production rates?

P23861, L13: According to Fig. 6 the SSS-oxalate relationship is not similar to the SSS-nitrate relationship

P23862, L1: Its difficult to make from Fig. 6 but the comparison of the absolute concentrations seems to suggest that at times the DEA+DMA concentrations were substantially greater than the WSON concentrations. Please verify and if true, discuss the implications.

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P23862, L19: The Kz were calculated with the parameterisation against wind speed in Fig. 1., and therefore, the uncertainty in the flux was not just "down to the uncertainty of the gradient".

P23863, L26-28: Does "...best fitted to the line" mean best fitted with a linear function? Was the linear function fit to all the data, or just the positive flux points? The wind speed range over which the relationship is valid should be stated. Even if the negative flux points are not included in the fitting process, they should be shown on Fig. 8 since they are discussed quite extensively. Do the negative flux points correspond to the WIOM_removal concentration profiles in Fig 3? Also, the equations referenced here do not seem to correspond to the text. Finally, it is not clear to me why these processes would result in WIOM flux having a linear dependence on wind speed?

P23864, L19: Given the uncertainties in the flux calculations, I think it is dangerous to present a parameterisation of the WSOM flux-wind speed relationship without discussing why or how WSOM removal depends on wind speed. Some discussion of a physical basis for such a relationship is required to support the parameterisation. Concerning the details of the calculated WSOM fluxes, given that it is suggested that "a significant fraction of WSOM is in fact processed primary WIOM", can it be safely assumed that the surf zone had no impact on the 3m concentration measurements? What are the consequences of assuming the contrary and not using the 3m measurements?

P23865, L24: Provide references for statement concerning models and their overestimated mass concentrations

P23866, L7: Provide references for temperature effects on sea spray aerosol production.

P23867, L10: As per comment above, the equation for OMss represents the mass fraction of OM in sea spray, not the OM enrichment factor. Also, what was used to represent OM? I assume only WIOM as was implicitly done in Eq. (3), but should be explicitly stated. Do the relationships with wind speed and Chl presented in this section

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change if some fraction or all of the measured WSOM is assumed to be associated with sea spray (e.g. formed from the processing of primary WIOM)?

P23867, L14: Details on how these Chl a concentrations were measured/calculated should be provided here or in the Methods section. If Chl a concentrations have been measured/calculated, could these be used to test the hypothesis resulting from the different WIOM concentration profiles (that the profile shape depends on the degree to which regions of high biological activity overlap with the flux footprint region P23858, L15-29)?

P23867, L15: Suggest it would be more appropriate to report the coefficient of determination (R^2) directly rather than the coefficient of correlation (r) so the reader can immediately see the proportion of the variation in OMss explained by the fitted relationship.

P23867, L17: It seems that a comparable fit could be obtained by fitting a linear function to the OMss vs wind speed data. More broadly, the analysis in this section and presented in Fig. 10 is an incomplete way of investigating the dependence of OMss on wind speed and Chl a since it appears there is some correlation between wind speed and Chl a (Fig. 10). The questions asked here should be answered through a multivariate analysis.

P23878, Table 1: Please include the total number of hours each sample was sampled over.