

Reviewer 4

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 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.

Response

A paragraph was added explaining the rationale of the approach.

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.

Response

The different distances of the flux footprint arise from emissions contributing to the concentration at different heights. The flux footprint of the 90% concentration differential between 3 and 10 meters is 0.2-1.2km while the footprint of the 90% of the difference between 10 and 30 meters extends to 5km (Figure 1, Ceburnis et al. 2008). The remaining 10% of the contribution extends well beyond 5km, so the correct distance should be 0.2-10km and is now consistently corrected. With regard to condensation potential, the time required for the air parcel to cover 10km distance is about 15min which is more than sufficient to achieve gas-aerosol equilibrium (e.g. Meng&Seinfeld, 1996; O'Dowd et al. 2000). The above sentence has been added to text.

2) How were the positive concentration gradients established, and why do some secondary species display positive gradients 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?

Response

Addressed along with the previous comment.

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.

Response

Indeed, no physical meaning is behind the curves. Having not used the lowest height for primary gradients due to potential surfzone impact, gives another reason to abandon curved profiles. All profiles have been changed to connected lines.

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.

Response

In order to avoid crowding of the graphs the uncertainty values of all fitted parameters were summarised in Table 3.

** 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.

Response

Thanks for pointing this out. Discussion on of the seasonality has been added as a chapter 3.5.

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

Response

References provided.

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

Response

Absolute concentration ranges for each measured chemical component are summarised in Table 2.

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?

Response

The variance of different profiles around the mean normalised concentration is presented as the standard deviation. When it comes to calculated fluxes based on individual profiles, measurement uncertainties propagate into flux uncertainties according to the law of error propagation as explained in chapter 2.5. There is no decision to be made here: an average should be presented with the standard deviation, while individual fluxes should be accompanied by propagated uncertainty including all the measurement errors.

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

Response

A dedicated chapter 3.5 has been added to discuss observations of the seasonal patterns.

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

Response

Done

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).

Response

If the values are normally (or close to normally) distributed they can be meaningfully averaged. The test here revealed that the K_z vs WS relationship with the horizontal wind did not change going from high resolution data to the ones averaged over long hours. A discrepancy may have been expected if the K_z values were varying differently at different wind speeds (e.g. due to changes in boundary layer stability), thus preventing meaningful averaging. However, the reviewer was right pointing out that was not a test of normality and was substituted by "consistently distributed" which is not an inherent condition due to several factors involved in K_z vs WS relationship.

The reviewer is right that the variance in K_z around the mean value indicated the uncertainty which propagated into flux uncertainty which is now stated in the text.

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

Response

Done

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

Response

Our interpretation is based on a statement that the effect is considerably smaller at higher levels than at the levels below. Norton et al. summarised that "... internal boundary layer development has **reached** between 10 and 15 m at the sampling location. In the north-westerly sector there is **some** indication that the stress at 15 m has been perturbed, though the effect is considerably smaller than at the levels below."

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?

Response

Done

P23856, L6: The equation for OMss represents the mass fraction of OM in the sea spray, not the organic enrichment factor. Enrichment factor is the ratio of OM fractions in 2 different media (e.g. $EF = OM_{ss} \text{ in aerosol} / OM_{ss} \text{ in seawater}$) and represents the degree of organic enrichment in one medium relative to the other.

Response

The reviewer is right and we are currently replacing our historical usage of enrichment factor to fractional contribution of OM in all our future papers. The text was corrected accordingly.

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.

Response

WIOM suggestion followed. Regarding the derived Equation, here is the breakdown:

$$\begin{aligned}\frac{\delta OM_{SS}}{OM_{SS}} &= \frac{1}{\frac{WIOM}{WIOM + SS}} \sqrt{\left(\frac{\partial OM_{SS}}{\partial SS} \delta SS\right)^2 + \left(\frac{\partial OM_{SS}}{\partial WIOM} \delta WIOM\right)^2} = \\ &= \sqrt{\frac{\left(-\frac{WIOM}{(WIOM + SS)^2} \delta SS\right)^2 + \left(\frac{SS}{(WIOM + SS)^2} \delta WIOM\right)^2}{\left(\frac{WIOM}{WIOM + SS}\right)^2}} = \\ &= \sqrt{\frac{WIOM^2(WIOM + SS)^2}{WIOM^2(WIOM + SS)^4} \delta SS^2 + \frac{SS^2(WIOM + SS)^2}{WIOM^2(WIOM + SS)^4} \delta WIOM^2} = \\ &= \sqrt{\frac{WIOM^2 \delta SS^2 + SS^2 \delta WIOM^2}{WIOM^2(WIOM + SS)^2}} = \sqrt{\frac{SS^2}{(WIOM + SS)^2} \left(\frac{\delta SS^2}{SS^2} + \frac{\delta WIOM^2}{WIOM^2}\right)} = \\ &= \frac{SS}{(WIOM + SS)} \sqrt{\left(\frac{\delta SS}{SS}\right)^2 + \left(\frac{\delta WIOM}{WIOM}\right)^2}\end{aligned}$$

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.

Response

Corrected

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

Response

Corrected

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.

Response

It is pretty clear that nitrate and oxalate profiles are different from sea salt at the lowest levels. While sea salt concentrations are statistically different at all three levels (note error bars), nitrate and oxalate profiles are not so different at 3 and 10 meters.

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?

Response

The reviewer correctly noted that deposition of large particles is considered inconsistently. Sea salt particles at the lowest level were the freshest having the closest flux footprint and, consequently, got the least amount of condensable nitric or oxalic acid compared to higher levels. Text was changed accordingly.

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

Response

Done

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.

Response

Done. Also each category is now discussed in seasonality chapter 3.5.

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 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.

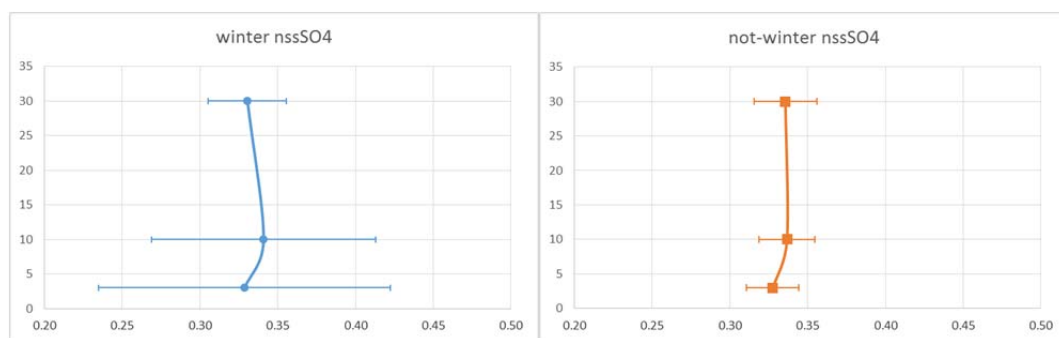
Response

The issue is now discussed extensively in the seasonality chapter 3.5. The corresponding fluxes resulting from removal profiles are also discussed in chapter 3.2.1.

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

Response

This ambiguity is, indeed, reflected in the error bars (Figure below). If we separate winter cases from the rest we obtain much more meaningful non-winter profile similar to the one presented by Ceburnis et al. 2008 when there were no winter samples. We chose, however, not to treat samples selectively.



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

Response

Calculated NH_4 is the required amount of NH_4 to fully neutralise NSSO_4 and NO_3 . Figure 5 is now properly introduced and discussed.

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

Response

The fact that aerosol appears more neutralized at 30 m than at sea level, might indicate that the process of sulphuric acid neutralization occurs more effectively through cloud-mediated reactions than through gas phase processes. Gaseous ammonia can be easily scavenged by cloud droplets (Seinfeld & Pandis, 1998) because of the high water solubility; there it interacts with the acidic sulphates already present in the droplets (solubilized CCNs or from oxidation of scavenged SO_2 , DMS, etc...) and when the droplets evaporate the processed aerosol is more neutralized than before. This process is more likely to happen at the top of the marine boundary layer, where clouds form, justifying the observed neutralization profile. Also a gradient in the vertical profile of ammonia could justify our observations, but unfortunately we do not have information on this. For this reason, this part has not been treated with more detail.

In order to make the text clearer, it has been integrated with this sentence: "In fact, if the neutralization of acidic sulphates occurred prevalently in clouds, after scavenging of gaseous ammonia into acidic droplets, this process would occur more likely at the top of the marine boundary layer, where cloud layers form, justifying the observed neutralization profile".

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.

Response

There was certainly enough time for nitrate, but when it comes to organic species the answer is not so clear. However, oxalate and then MSA were progressively more distorted suggesting longer equilibrium time than nitrate.

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

Response

8 profiles were discarded as incomplete, i.e. missing determined concentration at one or two levels.

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

Response

Done

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?

Response

The usefulness of the method for quantifying production rates is out of context and removed now.

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

Response

More than half of the points in the SSS-oxalate relationship would follow linear regression observed in SSS-nitrate relationship, hence, similarity. SSS-MSA relationship is very different from SS-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.

Response

It indeed occurred in some samples (<20%) and it is essentially due to the high uncertainty characterizing WSON measurements in aerosol samples, as already discussed in the manuscript (Par 3.1.2). An overestimation of amines by ion chromatography is less likely, even though it cannot be completely ruled out in principle, considering the very low concentrations typical of marine aerosol samples, that make ion chromatographic determination challenging. For those reasons, profiles of amines and WSON are discussed very carefully in the text. We would like to note that the two horizontal axes in the bottom right panel of Figure 6 (WSOC vs amines & WSON) are not directly comparable. In fact, WSON is expressed as mass of Nitrogen per m⁻³, while amines (sum of DEA+DMA) are expressed as a mass of compound per m⁻³.

A note was added to the Figure legend.

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".

Response

Kz values were, indeed, obtained using parameterisation in Ceburnis et al. (2008). This study, however, used actually measured Kz values for all the samples which is a very significant improvement over the previous study. Parameterisations in Figure 1 were examined for averaging purposes only.

Kz value of each gradient sample was the average of more than a hundred of half-hourly values and, therefore, its uncertainty was lower than the uncertainty of the gradient based on two measured concentrations. That is now explained in chapter 3 along with specific equations.

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 results in WIOM flux having a linear dependence on wind speed?

Response

The linear function was fitted to positive flux data only. Otherwise parameterisation would suggest constant removal at low wind speed which may not be true in all circumstances. The negative fluxes are now shown in Figure 8. Note that the flux was positive as well as negative at around 7m/s and was negative below 6 m/s. Interestingly, the negative flux dependence on wind speed was not very different from the production flux relationship. Indeed, the negative fluxes corresponded to removal profiles and were observed during late spring and early summer. References to the equation are typos generated by Copernicus system - (1) and (2) referred to processes not equations.

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?

Response

We agree that given the large uncertainty of the individual fluxes, particularly at high wind speed, the WSOM relationship with the wind speed could not be reliably derived and physically supported. Parameterisation was removed from the graph and discussed accordingly.

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

Response

Done

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

Response

Done

P23867, L10: As per comment above, the equation for OM_{ss} 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 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)?

Response

Only WIOM was taken into account in calculating fractional contribution of OM in sea spray. Notwithstanding the fact that a fraction of measured WSOM was plausibly associated with sea spray and formed by processing primary WIOM, quantitative assessment is beyond current methodology.

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)?

Response

The chlorophyll satellite data (daily, 1° spatial resolution) were obtained from GlobColour (<http://www.globcolour.info>). They result from the merging of Medium-Resolution Imaging Spectrometer (MERIS), Moderate Resolution Imaging Spectroradiometer (MODIS), and Sea-viewing Wide Field-of-view Sensor (SeaWiFS) data, using advanced retrieval based on fitting an in-water biooptical model to the merged set of observed normalized water-leaving radiances. A thorough description of the data treatment can be found in Rinaldi et al. (2013).

Regarding the dependence of fluxes on chlorophyll concentration is very tricky due to the fact that the flux footprint (not concentration footprint) is within 0.2-10km from the coastline and considering satellite spatial resolution and large errors associated with coastal interface. Some tentative links between WIOM profiles and biological activity are discussed in a new chapter devoted to the seasonality of fluxes.

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.

Response

Coefficient of determination was added and the text updated accordingly.

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.

Response

Both relationships were fitted and both explain 58% of the variance thereby suggesting an overlap. The excessive combined variance of 20% may be explained by the fact that the wind speed and chlorophyll-a are seasonally related – wind speed is higher during winter when chlorophyll-a is at its lowest which is simply a coincidence. Therefore, multivariate analysis won't solve the conundrum which can only be elucidated.

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

Response

Number of sampled hours each sampled was sampled was added to Table 1.