

Reviewer 3

I read this paper with some interest but ultimately was unclear regarding what new (innovative) insights were gained. The data are clearly presented but I did not see hypothesis testing being conducted or new ideas/methods being presented. Rather the data are used to 'confirm' existing knowledge – which to some degree is Ok but are these data (with all the associated uncertainties) moving us beyond the current state of 'certainty' in those expectations? The flux data set has been previously reported in Geever et al (2005) – though this current manuscript has a different focus.

Thus the summary of my review is: - The data set and analysis seem 'fine' but I doubt they are really well suited to address the profiles of different components (due to averaging, uncertainty etc). - The manuscript is in general clearly presented – indeed the introduction is a very useful review. . . BUT. . . - The manuscript – in my opinion – lacks the scientific impact that would merit publication in ACP.

Response

We believe it is fair to say that very few attempts of estimating aerosol chemical fluxes have been reported to date, so despite the lack of striking results it is useful to present a detailed account of the novel method and informing the community about its feasibility. This study is a significant advance over traditional eddy covariance method of estimating just particle number fluxes.

Explanation of this opinion is offered below: - If we look at the abstract the only result that is described is; "A strong power law relationship between fluxes and wind speed has been obtained not only for primary sea salt and sea spray, but also for secondary water soluble organic matter. The power law relationship between sea salt flux (FSSS) and 10 m height wind speed (U10) ($FSSS=0.0011U^{103.15}$) compared very well with existing parameterisations using different approaches." I think this is reasonable and expected based on previous work and theoretical predictions. (i.e. the flux should be a constant time U10 raised to some power that is approximately 3.). But it is also based on rather few observations and does not per se move parameterizations forward. – If we look at the conclusions it too presents only very "general" findings.

Response

The message not emphasized in the abstract is that the current method supports the notion that flux parameterisations should be attempted in ambient environment contrary to laboratory setting. We rewrote the abstract by emphasizing the novelty.

Details and specifics:

The inferences about the gradients is based on fifteen PM1 gradient samples collected during 13 month period (most of about 1 week in duration). Thus I suspect the uncertainty is rather high and much higher than the estimates given in the manuscript – e.g. gas-particle partitioning (on the filter) ought to be considered? Given the large amount of non-stationarity (again not considered in the uncertainty) can new physical insights be derived? Can 3 points in the vertical really be used really be used to derive robust information about the form of the profile? - The plot of dependence of the coefficient of turbulent-transfer K_z on the horizontal wind speed and normalized standard deviation of horizontal wind speed during April 2008, shows(as expected) K_z increases with increasing turbulence (wherein σ_u is used as a proxy) – is this surprising? Does it yield new insights? I don't think so.

Response

The uncertainty of a limited number of samples is impossible to estimate unless another study with more samples is undertaken. The number of samples is always limited independently of how large that number is. The uncertainty of derived parameterisations presented in Figures 7-10 as a shaded area was exactly for that purpose. An increase in the number of samples would reduce that area. We suspect the reviewer missed discussion on this topic in lines 16-25 in page 23856.

Regarding gas to particle partitioning it would equally affect samples at all heights thus having minimal impact on the gradient (not absolute concentrations). Non-stationarity can only be estimated if higher temporal resolution was available which was not the case in this study. However, we acknowledge the comment which will be included in the text. The Figure 1 was intended to demonstrate that despite non-stationarity and low temporal resolution averaging does not have a profound effect on the K_z and wind speed relationship therefore justifying purposeful averaging.

I am not sure the average shown in Figure 4 has any real meaning – it seems to convolute many processes and again I wasn't quite sure what physical insight one was suppose to derive?

Response

The average presented in Figure 4, indeed, does not have any physical meaning and the whole Figure 4 was removed containing nothing other than visual clues. Even more so that the concentration at the lowest level was left out from calculations as a precaution.

Minor point: I do not think the eddy covariance method was introduced by Buzorius (or indeed that he would claim to have introduced it); 'Eddy covariance method introduced by Buzorius et al. (1998)'

Response

Reviewer's comment made us realise about somewhat misleading sentence. Indeed, eddy covariance flux method was introduced in the 50th. However, in this paper we meant particle number fluxes which, indeed, were introduced by Buzorius et al. (1998).

Figure 5. A scatter plot of sulphate neutralisation by ammonium with respect to sampling height. I suspect a height-color scale/legend is necessary. But does one really expect a relationship here between NH_4^+ / SO_4^{2-} ratios in 1 week duration samples where within sample variability must be huge can one be sure this is representative of the atmosphere? And what real 'point' is being made here?

Response

Colour scale/legend has been added/modified.

The graph is not for expecting a relationship, but rather elucidating contrasting sulphate and ammonium profiles which is attributed to indirect derivation of non-sea-salt sulphate and varying neutralisation pattern along the height.

*Figure 6. Plots of sea salt and secondary species which resembled primary production concentration pattern: SSS vs. NO₃ (top left); SSS vs. Oxalate (top right); SSS vs. MSA (bottom left) and WSOC vs. WSON (also plotted as the sum of dimethylamine and diethylamine) (bottom right). ** what is the hypothesis that is being tested here? This seems a little like 'data mining' or exploratory analysis rather than a final 'result'.*

Response

Figure 6 is presented for explaining an apparent "primary" profile of nitrate and oxalate which is due to aforementioned species condensing or reacting with sea spray particles. MSA by contrast has the weakest if any relationship with sea salt. WSOC/WSON/DEA/DMA relationship is presented for exploratory purposes as these interrelationships have not been examined or discussed in the context of marine aerosol processes.

Figure 7 is again presenting the 15 points as confirmation of the power law presented by Ceburnis et al. (2008). I guess the uncertainty in wind speed represents the standard deviation around the mean but the vertical uncertainty bars should reflect the total flux uncertainty and surely should be much higher than are indicated here?

Response

The vertical uncertainty accounts for the uncertainty of the concentration gradient and K_z value, all calculated according to chapter 3. It must be noted, however, that the total uncertainty is not additive (which may be counterintuitive) due to the law of error propagation.

Figure 8 – how should one interpret the very large non-zero intercept?

Response

A significant non-zero intercept should be interpreted as the resultant net negative flux at very low wind speeds. That does not mean that the production flux becomes negative at low wind speed, but rather reflects observations when the production flux at very low wind speed in the gradient footprint area was smaller than the deposition flux of WIOM

generated tens to hundreds kilometres away. This interpretation has been incorporated into text.

Figure 9 – seems a little bit hard to read and also I am not sure really how to interpret it. Maybe removing parts of the graph where there are no data would help, maybe plot the data uncertainty would help too.

Response

The whole chapter 4.3 is devoted to Figure 9 the message being to demonstrate a disconnect between parameterisations derived from laboratory setting versus the ones based on ambient in-situ data. The part of the graph with no data from flux-gradient relationship is actually very meaningful and in particular the last paragraph of chapter 4.3 has been drawn from “no data” area.

Figure 10 is gain presented as ‘confirmation’ of past work but is presented without any sort of uncertainty and with many caveats.

Response

We do not understand this comment as Figure 10 is presented with all the uncertainties and even outliers explained in the top right graph (lines 1-4, page 23868). Figure 10 is presented not only as a confirmation of past work, but instead suggesting for the first time the underlying seasonal impact in the three-parameter relationship of fractional OM, chlorophyll and wind speed (lines 24-27, page 23867).