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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Primary marine aerosol emissions: size resolved eddy covariance measurements with estimates of the seasalt and organic carbon fractions" *by* E. D. Nilsson et al.

Anonymous Referee #3

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This paper introduces a promising approach to resolve marine aerosol fluxes using eddy covariance. The first part of the paper merits publication on this ground. However, later on the paper moves into speculation and questionable assumptions that are not based upon measurements but plausibility arguments. A number of specific concerns are raised below. These arguments are largely built upon measurements of Cavalli et al. data that also forms a basis for ODowd et al. These report unusually high concentrations of OC (60%) in clean marine aerosol that are used here to guide hypotheses. However, similar large concentrations have not been seen to my knowledge and most report values near 10%. These referenced measurements were subject to potential influence from continental long range transport and recent measurements

(eg. James Allen, paper 16A.4, AAAR meeting, Reno, 2007) have not found these high concentrations in clean Atlantic air carefully screened for pollution.

This paper takes great efforts to try and harmonize observations with hypotheses of an organic encapsulated aerosol after the referenced Ellison et al. paper. The Ellison paper is an intriguing idea but, as presented here, the data and instrumentation in this paper do not appear adequate to address this issue without tenuous assumptions. Consequently, I think this part of the paper appears premature and should be deferred unit more complete and unambiguous measurements can be brought to bear The use of English throughout the paper is often awkward or misleading and very difficult to follow. One of the authors is the former editor of JGR and it is hard to believe that the text was read carefully. This must be done before resubmission. There are numerous other issues of a specific and at times critical nature outlined below. These should also be addressed before resubmission.

Abstract: Improper English such as (In consistency) or (It is speculated)or (This predict) here and throughout the text . After - It is speculated - the abstract does report speculative behavior that is not a finding and should not be in abstract. Needs careful edit for language and this should not be a task for the reviewer and will not be done here.

P 13347 L14-22 Not relevant to paper, please delete

P13350 The authors refer to the MA03 (laboratory tank measurements), CL06 (coastal surf measurement) and GO03 (guess work) as parameterizations. However, the first two are based on direct measurements while the latter is a extrapolation to small sizes of earlier Monahan data for larger sea-salt. [Also, see text on pg 13352 L 12-24]. Such extrapolation was cautioned against by Monahan and has been reiterated since. This paper eventually goes on to say that the arbitrary tuning parameters for GO03 do not fit the data. I believe that including the GO03 extrapolation with the MA03 and CL06 measurements for the bulk of the paper is not warranted (except perhaps later in the

ACPD

7, S5864–S5874, 2007

paper where its limits are discussed). Rather, a more relevant reference is that of the recent book by Lewis and Schwartz (LS) (surprisingly not in the references here). LS does not discuss the sizes smaller than 0.1um but, as these are not sized in this paper either, comparisons to LS sizes should possible and included. The extensive LS evaluations of prior measurements yields a canonical expression for the sea-salt flux (and variability) that is a more suitable benchmark for comparisons here even though it does not extend to smaller sizes.

See Lewis, E.R., and S.E. Schwartz (2004), Sea Salt Aerosol Production: Mechanisms, Methods, Measurements and Models, AGU Monograph Series 152, 413 pp, American Geophysical Union, Washington D.C.

L19 Although they mention agreement with a 100nm mode in the co-author Martensson tank studies and two others (Keene et al.-supposedly in press; and Tyree et al, not listed in references) they do not mention another co-authors data (ODowd, 2004) that reported smaller sizes near 40nm at this site.

P13351 L 18 they say, We could see from the beginning that MA03 produced a realistic number of particles compared. Here is one of the far too many places where a qualitative comparison is made that is totally un-interpretable to the reader. Moreover, the authors have no size resolved data below 0.1um and their integral value looks to be about a factor of two higher than the highest MA03 data over this range. What is meant by realistic in this context? If it is worth saying qualitatively then make the quantitative comparison to the models promised in the abstract.

P13353 they claim in sentence that (It is possible MO86 - had all the tank data been used). As this claim differs from claims made by the authors of MO86, this claim requires at least a reference as personal communication from the MO86 authors.

P13354 L1 they say, We will let the results determine if any given parameterization is valid and decide what direction to go next (??) Here the authors presume to use their paper as a validation and test of various previous studies being compared. This is

ACPD

7, S5864–S5874, 2007

curious as (unlike the MA03 and CL06 experiments that use so-called modern instrumentation this paper has no size information below 0.1um (or 0.13um if you throw out their lowest apparently unreliable size). Moreover, the error bars included in their distributions clearly underestimate the actually uncertainty in their measurements (given the adjacent point size variation) and the fact that comparisons to other size resolved fluxes do not include the published uncertainties of those fluxes. Consequently, this is not an acceptable validation in any standard sense.

L24 Wind rotation and time lag in sampling line. What were these values and their uncertainty and did they reasonably reflect the topography concerns and sample flows etc. One would expect the wind rotation to possibly depend upon wind speed, wind direction and topography differences in various directions direction. What are uncertainties and the implications of propagating these uncertainties?

P13355 L9 Dp it the diameter as measured by the OPC L10 (should be the diameter of the remaining sea-salt particle) Do the authors also mean to include residual organics stable at the temperature used – as evident in various cases for continental OC?

P13356 L10-18 IMPORTANT OPC issues that must be clarified.

The OPC is absolutely central to this analysis and needs more discussion on how the OPC was used and calibrated? IMPORTANT: what was the ambient RH and the operational RH and temperature at the sensor volume after cooling down from heater. If the sensor volume was unheated then, if air cools back to near to ambient temperature (rapid and common), unless water vapor is removed in some way the RH will return to ambient values and the sea-salt will commonly grow and be wet when sized. This would change both physical and optical size and refractive index. If vertical velocities are also correlated with ambient RH fluctuations (very likely) this will also bias sizes and flux. Similarly, unless dry, the total aerosol sizing will also vary with RH. Please provide clear details on what steps were taken to ensure sensor RH stayed dry relative to

ACPD

7, S5864–S5874, 2007

ambient RH for BOTH heated and unheated cases. This generally requires deliberate efforts. As it is later assumed that the results apply to dry sizes, this issue needs to be clearly resolved. Wet sizing of total could account for much of their 3.7 factor claimed for total aerosol relative to sea-salt.

The first channel of this instrument often has overcounting problems reported due to noise. The data show later (Fig 4) suggests this may be a problem here. Was this behavior evaluated?

P13357 TOWER issues L 4-12 The prior referenced tower gradient measurements and the decision to mount the sensor as high as possible suggests that gradients exist in the vicinity of the inlet. The comment that even at low tide influences were detectable at the tower suggests that this could be even more for coastal generated sea-salt at high tide. This is important because if a significant coastal and organic influence is present at Mace Head then it will not have the same behavior as wind generated sea-salt offshore. In the next paragraph they go on to say that measurements were (intended) to be made above the internal boundary layer and it (appears) high enough to be (close to open sea conditions). What was the tidal range during this experiment relative to the low tide measurements mentioned? As the authors had the instruments necessary to confirm a gradient and its variability during this extended measurement period, why was this not done?

THIS IS IMPORTANT BECAUSE IF THE MEASURMENTS SHOWN ARE BIASED BY COASTAL BREAKING WAVES (Fig. 1) THEN LINKS BETWEEN FLUXES AND WIND SPEED WILL NOT REPRESENT OPEN OCEAN CONDITIONS OR A WIND SPEED DEPENDENCE. THIS WOULD UNDERMINE THE COMPARISON TO OTHER DATA SETS ON A WIND SPEED BASIS.

This is a real concern as on P13363 L 5-9 they say, It is worth noting in Fig3h that aerosol number concentrations of either the CPC or OPC do not follow the wind speed variation. The CPC aerosol concentration is even anticorrelated with wind speed.

ACPD

7, S5864–S5874, 2007

THIS ANTICORRELATION IN CPC BEHAVIOR WOULD BE EXPECTED FOR LOCAL SHORE INFLUENCE ON TOWER DATA Though often variable, the OPEN-OCEAN source is expected to correlate with wind speed. However, coastal breaking waves are topographically forced and not driven by wind speed (may depend on waves, swell, tide). Hence, increasing wind speed dilutes this coastal line source and would account for the inverse dependency noted and suggesting sea-salt at the inlet height can have a shoreline origin.

P13359 CORRECTIONS Thermophoretic losses (and higher velocity) in heater tube will be different than unheated tube? OPC calibration uncertainty not included. Possible wet aerosol mentioned earlier not included.

P13360 change (the errors) to (the counting errors). Size dependent OPC sizing and calibration uncertainties etc. are not included.

P13361 L 3-13 Awkward English and structure. Rephrase. Also, how large is this natural variation? Specifically, how variable were measured fluxes under essentially equivalent environmental conditions during the experiment period? Show variability bars for a given wind speed etc.

Figure 2 should have same scale for x-axes. What is meant by (current) number flux. The difference in the peak for the frequency spectra appears to be about a factor of two and is not explained. What is the physical meaning of this? Does it imply the so-called sea-salt and total aerosol are transported in different size eddies? If so, how is this understandable?

L20 In principle the CPC is a simpler measurement as it is not size resolved but has less issues associated with fluctuations in humidity and size (see above). Hence, rather than invoking a diffusive loss term to explain difference, could it not be that the CPC is more correct and that the higher upward flux for sized aerosol may be linked to such issues?

ACPD

7, S5864–S5874, 2007

P13362 Here a more careful comparison is needed. Statements like (to low) and (fair agreement) need to be quantified relative to uncertainties. The issue is whether this new EC data provides robust constraints on the MA03 and CL06 flux estimates. Hence the full uncertainty in all EC fluxes need to be revealed along with the uncertainties described in the MA03 and CL06 papers. The Nillson parameterization (not previously discussed is shown) and said to disagree from MA03 by a factor of 2 or 3. However, this appears to be an average of differences that exceed a factor of 5 and many cases where points agree with both MA03 and CL06. This one day is not a validation. No other quantitative differences are described (approximate, fair, low etc. are the terms used.). Real error bars, variability and related overlap are not discussed. Such data needs to be averaged over similar wind conditions for various days in order to identify systematic differences.

P13363 L20 they say (for all but the lowest wind speed in Fig. 4a the MA03 predict(s) the observed flux size distributions very well) Fig. 4a clearly shows problems with the measurements that provide some indication of real uncertainties. “some of the relatively larger scatter should originate from discrete counting errors”?? How is the apparent huge variability for adjacent sizes explained? Fig. 4b,c are not convincing or consistent regarding MA03 or CL06 while Fig 4d does appear to agree better with MA03.

P13363 L20-25 Fig 4 The EC data is unusually scattered in adjacent sizes at lower wind speeds indicating uncertainties much greater than those claimed. Even so, they are typically far higher than differences in MA03 and CL06 except at higher winds where it appears to agree best with CL06. The authors claim this points to a problem with all other fluxes - except their EC flux. However, their enhancement may reflect the influence of coastal breaking waves relative to open ocean waves, as mentioned above. These would raise concentrations significantly and the lower winds may enhance vertical mixing to tower height. In view of earlier TOWER comments this appears to be a possible explanation that should be discussed.

ACPD

7, S5864–S5874, 2007

More generally, why are only these short time periods selected for comparison at the 4 indicated wind speeds? Given the duration of this experiment one would expect numerous examples that could be averaged for each wind speed regime. This would provide a mean and standard deviation of the EC results for each wind speed that would provide some clearer measure of uncertainty.

P13364 L28— The authors claim their fluxes compare well with MA03 but claim that comparisons to CL06 (do not fall out well)(??) with their data. What comparisons – these and statements of (close to), (slightly above), (favorable) etc. abound in the text but true regressions or even % differences over specific ranges etc. are rarely mentioned? PLEASE avoid vague qualitative claims and actually make some quantitative assessments over the size distributions with RECOGNIZED OVERALL UNCERTAINTIES for each approach included. Only differences greater than expected uncertainties of the combined approaches merit a discussion of differences (or claims for validation). Fig 4 does not clearly demonstrate better agreement with MA03 or CL06. If anything, these appear to agree better with each other than with EC. Also, there are the tower issues and its influence on appropriate wind speed and the poor larger particle performance of the EC method to be considered.

P13366 L10 Fig. 6 they say (CL06 have a too low slope (English)) Both the EC data and the data of MA03 are recognized in the text to poorly characterize larger particles, it follows that both are likely to have too steep a slope at larger sizes (undercount). See beginning of section 3.7. Hence, their (favorable) agreement (high slope) does not imply that these are correct or that they can be used to validate in invalidate CL06 via. their slope.

P13366 Here the paper begins to move away from the science of the measurements into speculation. I suggest the authors address the issues raised above and wrap up the paper at this point. More robust measurements will be needed to explore the speculations raised. I refer to the issues of the actual RH in the OPC sensing volume for heated and unheated aerosol could have large effects on the sizing and interpretation

ACPD

7, S5864–S5874, 2007

of sea-salt and total aerosol discussed. The other issue of shoreline sea-salt contamination will undermine the wind-speed classifications, particularly at low winds. This is where the unreasonably large differences in EC vs. other fluxes arise.

The rapid measurements made should be able to identify rapid excursions associated with shoreline waves and foam compared to the less variable open-ocean whitecaps. Was this evident in the data before considering fluxes?

These issues need to be clarified before suggesting their measurements indicate a layer of emulsion and organics are out there that influences the sea-salt production under low wind but becomes ruptured under high winds in order to generate orders of magnitude more mass on the sea-salt than has been previously detected under low wind.

P13367 L9 I do not understand what is meant by (but on a generally higher level than these).

P13368 Again speculation on organics that were not measured simply to try and explain curious behavior’ How about measurement issues?

P13368-9 they say (For sea-salt the aerosol number flux is well correlated…..for total aerosol the correlation is much smaller) These correlations appear to explain less than 50% of the variance for sea salt (P13368) and considerably less for total aerosol even after excluding the anomalously high values under low wind speeds. This raises the question of how this impacts comparisons (validation?) of these data with MN03 and CL06 based upon a specific wind speed parameterization.

P13369 Here we are told that we will be comparing sea-salt and total fluxes that are neither concurrently sampled, not from the same season, and not for the same wind speed (somewhat different average wind speeds of 10 and 8.3 m/s)!!! This will be a factor of 2 difference in mean flux using the authors wind speed dependence. But then they go on to say the higher winds yielded the lower flux (this could be expected

ACPD

7, S5864–S5874, 2007

for a coastal breaking wave but not likely for open ocean) (see below). Since rather sweeping conclusions are being built on this comparison this require a great leap of faith by the reader to believe this is acceptable. More faith than I can muster, but this is not the only concern I have.

P13370 A factor of 3.7 change in diameter in response to heating over the 0.1 to 1.0 um size range is large and apparently not consistent with the smaller size displacement evident in Fig. 9. Even so, figure 10 tends to show the largest shift at smaller sizes. However, in section 3.3.2 they claim it is reasonable to assume that CPC particles do not shrink below 11nm. Why? One of the authors (O’Dowd) recently published the summer unheated size distributions with a mean peak near 40nm and dominated by OC in the less than 0.1um sizes. If this distribution were heated it would appear a large fraction would lie below 11nm. Hence, this claim needs to be justified and harmonized by these observations otherwise there is little to support the CPC data as representing a sea-salt flux.

The authors claim that this represents good agreement with the Ellison model (P13374). However, Ellison claims their model should result in organic preferentially residing in the 0.1 to1.0 um range (as characterized by the EC measurements here). They estimate OC at 10% the mass of 0.1um particles and 1% the mass of 1um particles, much less than implied by these EC measurements. During the same time period of the NAMBLEX expt. reported here the results from an aerosol mass spectrometer (AMS, Coe et al., ACPD,5, p11643, 2005) at Mace Head find pollution sources common and others (DallOsto et al, 2005) caution about pollution sources being common at Mace Head and elevated organics being commonly associated with them. Recent careful measurements with so-called modern instrumentation (eg. James Allen, paper 16A.4, AAAR meeting, Reno, 2007) have not found such high concentrations of OC associated with sea-salt in carefully stratified clean Atlantic air.

Also, if the aerosol contains the amount of water hypothesized here, the OPC sizing would be very different from than that of dry sea-salt aerosol. As no calibration issues

ACPD

7, S5864–S5874, 2007

were discussed for wet aerosol, it appears that no separate calibration was used for dry or wet aerosol (nor is it clear whether RH is known in the OPC sensing volume). Hence, the indicated total sizes and the size shift claimed appear ill defined and unlikely to be correct.

The authors need to demonstrate the consistency of these concerns with their observations and this discussion should be included in the text.

P13372 L15 This argument requires that the size distributions of the sea-salt generated with low OC (MA03, and presumable CL06) are physically far smaller (factor of 3.7) than the droplets encapsulated in OC produced from bubbles, as suggested here. Is there any other data from other investigators that support this conjecture? (Lewis and Schwartz ??)

P13379 Agreement with Middlebrook is claimed but that paper suggests organics are about 10% of sea-salt mass over the submicron size range. What is meant by agreement?

P13391 Clark should read Clarke et al. (2003) and is missing in refs.

P13394 Text does not describe lines and colors on plot.

I could go on but will terminate my review at this point.

In summary, although the process (Ellison et al.) being argued for miscelles etc. may be correct and though the authors clearly want it to be, the measurements as reported here are not adequate to prove it. Comparisons also need to be better quantified and realistic uncertainties included, as mentioned above. A lot of assumptions and estimates are made to show how the data might be consistent with this Ellison process. Nevertheless, the result is not very convincing and should be discussed in a separate paper when the evidence is more direct.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13345, 2007.