

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 #2

Received and published: 16 October 2007

ACPD-2007-0355

Primary marine aerosol emissions: size resolved eddy covariance measurements with estimates of the sea salt and organic carbon fractions

Review

This publication presents an aerosol flux dataset collected on Atlantic coast in Mace Head station, Ireland. Flux was determined according to eddy correlation method. Condensation particle counter (CPC) and optical particle counter (OPC) were used for aerosol detection. OPC delivered aerosol size distribution in the range from roughly 0.1

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

to 10 microns split into 31 size classes. Actual size boundaries for size classes were not presented. For the certain sampling time period aerosol entering OPC was preheated to 300C, and the measured aerosol size distribution was deemed to represent NaCl aerosol size distribution. During the remaining sampling time the OPC inlet was preheated just enough to keep relative humidity below 40%, and the measured aerosol size distribution was deemed to represent total aerosol size distribution consisting of sea-salt along with volatile components. In this review I call both distributions as hot and cold measurement. Note that both measurements were conducted with the same OPC during different days. Those are not side by side simultaneous measurements. CPC presented total aerosol number flux.

Measurement results showed significantly different fluxes per size interval for the same wind speed for hot and cold samples. Authors argued that primary marine aerosol is internal mixture of NaCl and organic material. The argument is presented using extended discussions with numerous references to publications that support abundance of organic material in oceans.

I welcome authors stand with their scientific message presented here that I find somewhat different from the mainstream. Presented conclusions appear somewhat over-stretched relative to the measurement dataset. This paper claims that primary marine aerosol has an organic component, that there is organic material attached to NaCl particle. The mainstream approach to ambient marine aerosol was too much concentrated on synthetic bath; approach. In the synthetic bath; it is assumed that primary marine aerosol consist of pure NaCl. In atmosphere, condensable gasses (organic, nss-sulfate) condense on NaCl modifying marine aerosol physical and chemical properties. Depending on season, location or particle size volatile component is dominant by nss-sulfate or organics. It was not clear why condensational process was not considered by authors in this study. I caution authors that experimental part of the study is not convincingly supporting their hypothesis. My caution has a lot to do with OPC application in measuring different chemical composition aerosols,

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

and eddy correlation requirements. Nevertheless results are presented in a manner of agreement with refereed publications where the importance of organics were highlighted (mainly Ellison et al paper).

Comments and questions on experimental part:

Chapter 2.4.1 introducing time constants for CPC and OPC. How those time constants were determined? Was it an issue that OPC has only 1 Hz resolution, not 10 Hz as accepted in EC? Was CPC time constant obtained from Buzorius (2001, Aerosol science and technology). If so, should be referenced. OPC applicability in EC. Authors note very high errors due to counting statistics in 2.5.1 chapter. Given estimates were 33% and 76% for 110 nm and 3.75 micron sea salt particles, with the error approaching 100% at larger sizes. I tried to recreate error estimates using values in figure 3, but did not find a value for $\sigma(w)$ in the paper. Assuming 1 m/s for the later, I got somewhat similar values as those presented in figure 3 d. My question is why error bars in figure 3c don't go down for data points presented on the left side of the plot? They go up, and on the plot with log scale, they should go down much more as in figure 3d. why they don't? Figure 11d. it is a ratio of sea salt to aerosol volume fluxes for particles larger than 0.4 micron. Considering that each of fluxes are detected with error bars somewhere from low tens of % to 100%, how meaningful is such ratio to present?

I did not see any discussion on refractive index. The refractive index for the heated seasalt aerosol, can be assumed as that for NaCl; for cold, I don't know what is a right value, but the most probably using the same value is not correct. Hopefully, different refractive indexes were used for the hot and cold measurement. It is important parameter compensating for different chemical composition particle reflectivity. What values were used?

Interpretation of the results.

There is limited information on footprint area. Page 13371, line 21 says gives 1km2 value for the footprint. I used <http://footprint.kljun.net/contact.php> model to estimate

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Interactive
Comment

possible footprint using 0.001 m roughness length, 300 or 400 m mixed boundary layer height, 0.2, 0.5, 1 and 2 m/s for vertical wind speed variance, and 2 to 6 m/s for friction velocity, model gives the distance at which the maximal contribution to the flux occurs, being from 1.1 to 5.8 km and 90% contribution to the flux occurs over the distance from 3 to 15 km. those are significantly higher values than authors reported. Authors could/should verify my estimates using actual data for vertical wind speed variance. If the footprint is indeed extending several kilometers, residence time in the atmosphere of aerosol emitted within the footprint area spans from several minutes to several tens of minutes and maybe an hour. It is long enough time for condensational growth to occur. Keeping this in mind, I can not refuse somewhat different dataset interpretation. Figure 8 shows that at low wind speed (<10 m/s) aerosol cold flux of particles larger than 100 nm (full OPC range) is not dependent on wind speed; while seasalt hot flux is dependent. I would argue that at low wind speeds residence time (time between the moment of primary emission and detection within OPC) is relatively higher compared to days with the high wind speeds (increased footprint for the higher wind speeds compensates only partly because roughness length increases). Therefore particles are able to grow by condensation from sizes smaller than 100 nm to the OPC detectable sizes. Mace Head is one of the sites where nucleation has been observed, indicating abundance of condensable gasses. The growth rate largely depends on the condensable gas concentration and the residence time. Therefore, the aerosol cold flux does not depend on wind speed (if wind speeds are low) but depends on number of particles growing from Aithen to accumulation mode. If volatile component removed (removes the amount of particles that grew to detectable sizes), flux depends on the wind speed, as is shown in the figure. At moderate wind speeds (10 to 15 m/s) the residence time is reduced along with the size change due to the condensation and primary emission rates are increased. Thus, we see dependence on the wind speed. At high wind speeds (>15 m/s), the residence time is further reduced, impact of condensational growth is minimal relative to the primary emission rates, and therefore seasalt and total aerosol fluxes curves approach to similar value (figure 8). Authors

Interactive
Comment

argument about depleting of organic layer on the ocean surface is not supported by direct measurements, somewhat speculative. At higher wind speeds, larger waves and more mixing at the ocean surface is expected. My interpretation does not require new assumptions and arrives to very different conclusions. Can authors find a mistake in my interpretation?

Minor comments: 1. line 1, 13348. there is a source of primary organic aerosol? Any direct experimental evidence for the "primary" part? 2. bottom 13349. it is strongly suggested primary organic carbon emission. How do we know that there is one? Impactor or other bulk measurements are not necessarily valid for this conclusion. 3. page 13350. tyree reference missing from the list. 4. line 2, page 13351 "modern aerosol instrumentation". The referenced study was done at least 5 years ago (published 2003), maybe modern word is no longer needed in referencing. 5. line 18. could not understand "we could see from the beginning";. Suggestion to rephrase. 6. line 14 to 17, page 13359. can not understand why penetrating fraction depends on whether sample is heated or not. The loss of volatile amount depends on aerosol, not the characteristics of the sampling line. "increase to <5%"; "should it be decrease to <5%? 7. line 26, page 13360 should it be Eq6? 8. figure 4 . y-axis has 5 orders of magnitude while measurement data spans over 2 or 3 orders, redraw. 9. chapter 3.4. refractive index issue. There is a high potential for large errors in determining particle size with optical instrument if incorrect index is used. What were value were used? 10. line 25-27, page 13367. if organics were on the ocean surface, emission rates still would depend on white cap area and wind speed via bubble bursting mechanism, is that right? Emission rate does not depend on the wind speed, when organic is already in the air. See results interpretation part above. 11. lines 9, 13372; shrinking by factor 3.7. it is very important to know correct refractive indexes here! 12. line 2, page 13378. OPC had errors higher 50% for larger particles. Is that still successful? 13. there is an earlier publication (De Leeuw et al., Production of sea spray aerosol in the surf zone, JGR, 105, 24, 29397-29409). How fluxes derived there are different from ones

measured in Mace Head? Both studies were conducted from the shore using optical particle counters, and size dependent fluxes were derived.

From the presented experimental material, it is not obvious that volatile component is made of organics. Could it been sulfate? Organic assumption was handed down from literature. It is probably correct assumption, direct measurement would help to prove it. As long as refractive indexes are not well determined, the amount of volatile component is also not determined correctly. I think the title should not mention organics, because current study did not measure organics directly. It was volatile component, while other (for instance Odowd et al review on marine aerosols) papers suggest sulfates and organics as main candidates. I did not get convinced that volatile component was primary emission and not condensation on seasalt based on arguments above. In overall paper is very good. has some new ideas. Experimental part needs to be strengthen, RI specified, figures corrected, and conclusions softened on organic part and include possibility of condensational mechanism if authors agree with my interpretation.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper