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Interactive comment on “Mediterranean nascent sea spray organic aerosol and relationships with seawater biogeochemistry” *by* Evelyn Freney et al.

Anonymous Referee #1

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The manuscript presents chemical speciation measurements from the oligotrophic Mediterranean Sea water bubble bursting experiments and the source apportionment of marine organic matter (OM). It aims at relating the marine organic concentration and speciation to sea water composition and presents parameterisations for different types of organics. This is potentially very valuable data set, but lacks some better analysis and discussion. Three major findings like refractory OM, OM source apportionment and finally parameterisation are little convincing as detailed below.

Major comments: The presence of refractory OM is not proven, but just speculated. The evidence in the paper can alternatively point to some problems with the ACSM instrument or, more likely, to potential instrument overload with the sea salt. Until this is proven incorrect, the refractory OM origin is little convincing. Especially that

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the missing fraction is increasing with time and/or the sea salt load. High sea spray concentrations exceeding 30 μg/m3 are not representative of ambient sea spray and may well overload the ACSM heater, making measurements non quantitative, thus, causing the registered disagreement with the filters. Was there any relation to RH? Why there is such variation in the sea salt concentrations if these are not ambient, but bubble bursting experiments?

Moreover, an origin of sulphate in the ACSM measurements is not discussed, is it sea salt SO4? Why there is a variation in SO4 fraction with measurement time if it supposedly comes from the sea spray with constant SO4 fraction? Also, why such a big difference between filter SO4 and ACSM measured, refractory? Discussion is required to explain these issues.

Figure 2 and Figure 3 clearly show that the missing fraction goes up with time and after the high total loadings (grey goes up just after the black goes down). The agreement with DMPS deteriorates after high sea salt loading. Pointing again to overload rather than refractory OM. Also the feature observed and discussed in lines 323-324 might well be due to overload rather than the theory presented that would in any case need more discussion and evidence than it is presented now. How the OM discrepancy between filters and ACSM changes with time, is it like one with DMPS for which agreement is worse after high sea salt loads?

Secondly, source apportionment section lacks any detail and objective factor selection information and justification. Why 4 factor solution and not 3 or 5 or, maybe, 6? Correlations with the external reference profiles are very weak and do not exactly justify the factor selection. But even that (correlations as a base for factor selection) is only stated in the text, but not described at all. Factors as they are now might be a result of factor splitting (the lack of oxygenated m/z in some profiles, like MSA, but appearing in much higher contributions in others, like OOA). What is the justification for splitting MOA and POA? They both correlate well with leucine and valine, could they be from the same source? Discussion around this point and quantitative statistical reasons of separating them is lacking. OOA correlation with reference profiles is neither presented nor discussed. High O/C ratio observed in OOA might well be due to wrongly separated factor. What is the justification for removing sea salt ions, is the instrument mass resolution high enough to assure that only sea salt ions were removed? If it is unit mass resolution, you have removed the associated organic contribution. Wouldn't it be better to have these in the PMF and separate a sea salt factor with corresponding explanation of its origin? Justify the removal of m/z 29 as opposed to downscaling.

Moreover, if MSA was indeed produced by bubble bursting, this could be a significant result, but, again, lacks comprehensive analysis and discussion. Could it be that you have detected some MSA precursors in the water like dimethylsulfonium propionate? or something else? What is the strong evidence for MSA presence? Poor MSA correlation (<0.2) to external profile is very unconvincing for this factor selection in this particular PMF solution. Is 0.2 even significant? Why a diurnal MSA trend was not observed if it was indeed from water oxidation? It is not even discussed along other diurnal trends in Figure 5, why? Discuss the possibility of oxygenated MSA m/z being wrongly attributed to OOA and the consequences on the MSA factor and the overall PMF results.

Finally, the parametrisation of OM was not shown in detail and lacks validation to be considered by a modelling community. The reproduction of the measurements in the manuscript is not shown. What fraction of variability is explained? Fractions of OM are not shown anywhere in the manuscript, just mentioned briefly in this paragraph.

The overview of previous chamber experiments related to marine aerosol in the Introduction is quite shallow, I agree that there are only few studies to date, but even these few are missing in the Introduction.

Is the standard CE applicable here? Provide assumptions/basis for this (lines 271-272).

The introduction of jet drops at lines 445-447 is questionable. Needs better discussion. Would jet drops not produce larger particles than those that are measured with PM1 instruments, both online and offline? Also, the different POA time variation could occur

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due to sea salt replacement by primary organics in PM1, which would cause these different sea salt and OM time trends (higher OM enrichment or fraction would mean less sea salt in the sea spray, where higher OM result in lower sea salt while overall sea spray concentration remains the same).

Discussion at lines 328-330 is not elaborate enough. To me, the WSOM shows a very different trend to OM from ACSM. What causes the ACSM peak around 21-25 May, which is completely missed by the filter analysis? The difference in time trends makes me question the fact that online and offline techniques were measuring the same thing, can you at least show one compound that has a good agreement between the two techniques? Why WIOM has fewer points than WSOM? Explain this in the manuscript.

Specific comments: Abstract states 15 min time resolution or ACSM while it is 10 min in the text (line 244). Be consistent, and state what was the real time resolution.

Provide reference for statement on lines 49-50 on the sea spray emissions

Fig 1: provide units for Chl-a and POC

Line 147: what was the time resolution for these measurements? Also, for other measurements of water composition like Synechococcus, PicoEukaryotes, NanoEukaryotes, Coccolithophore, Cryptophytes, etc.?

Lines 225-226: provide more details on acidification before analysis or provide an appropriate reference to the method

Lines 287-288: correct the sentence, it has ‘showed’ and ‘is’ in the same sentence

Line 312: why the real sea salt density was not used for the sea salt, which is 2.165 rather than 1.75. What other inorganics were there?

Figure 4c: correct the labelling, it is either shifted or labels are given to minor m/z, difficult to read this figure.

Line 371: provide the H/C value

Lines 414-415: I'm confused with this statement, do you refer to satellite based or concurrently measured Chl-a or both?

Line 415: I question the use of appropriate reference here as, to my knowledge, Rinaldi et al. 2013 did not discuss these issues. Provide the correct reference.

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