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Atmospheric Chemistry and Physics Discussions

Interactive comment on "North Atlantic marine organic aerosol characterized by novel offline thermal desorption mass spectrometry approach: polysaccharides, recalcitrant material, secondary organics" *by* Michael J. Lawler et al.

Anonymous Referee #2

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The study by Lawler et al. is dedicated to applying state-of-the-art instrumentation to elucidate sea spray composition over the North Atlantic with a particular focus on transferrable water soluble organic species and their relationship to ocean biological activity. The main idea of the study to utilise TDCIMS is innovative and producing new insights into the subject. The main problem with the paper and forthcoming conclusions is the number of samples which makes it difficult in arriving at robust inferences due to inherent natural variability temporally as well as spatially. The authors did their very best in trying to squeeze as much information as possible from the data analysis

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and fairly interpreting their findings. However, due to scarcity of data the conclusions are rather vague and tend to overly rely on previous literature findings and seeking commonality, which is only natural given limited sample bank. I am not sure if the paper should rather be published in Atmospheric Measurement Techniques which would be a more suited medium for application of innovative techniques and somewhat limited dataset. ACP is instead reporting scientific advancements which are quite limited in this study due to overarching limitations. As an example of difficulties the authors confronted in terms of robustly derived conclusions is poor statistics. How can basic statistical variables be derived from e.g. 3 samples? Overall, the paper is written very well and follows clear structure, so apart from vague conclusions (not of authors fault) can possibly be published in ACP after addressing the comments.

Comments in their sequence:

Title I think the title should be amended to "...thermal desorption mass spectroscopic approach:..." Later in the methods it is worded exactly that way.

Line 89. It is unclear whether submicron fraction overlapped with <180 nm fraction or was it separate 180-1000nm size fraction?

Line 95. The criteria are appropriate, but not very conservative. Typically, CN concentrations in clean marine atmosphere are <1000 cm-3, except for new particle production events. Radon concentration is typically more like <200mBq/m3 and BC<30ng/m3 (but depends on the measurement method and instrument). While the differences are not large, but it is important to observe that the increase in CN is not associated with the increase in BC or radon, which would immediately suggest diluted continental outflow or ship own exhaust. 48 hour trajectories are good, but should be checked if they stay in the boundary layer or were affected by large scale subsidence. In summary, I would argue for a more conservative and integrated approach, because typical marine background is very low and can be easily perturbed by even by sporadic pollution events including own ship (stacks or various exhausts).

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Line 110. How many samples a subset consisted of? It is not clear how many "clean marine" samples were preferentially chosen. Later in the text and figures can be seen that probably 27 "clean marine" samples were analysed in two size fractions each. How many corresponded to Sea sweep and how many to the ambient? All that information should be stated right at the beginning. At the moment the sample set is completely under described.

Line 149. NaCl fraction in sea salt is about 70%. What was the reason not choosing sea salt standard from Sigma-Aldrich or similar company? Na may respond differently in a more complex matrix in the instrument, but having sea salt matrix would certainly be compatible with sample extracts.

Line 153. PMF value and purpose was developed for large datasets/matrixes. Having only a handful of samples what was the purpose of statistical multivariate technique, when it is well known that PMF output (and of every statistical technique) is more reliable with large number of samples? I believe rich spectroscopic signatures were the reason to analyse the results statistically, but still highly non-symmetrical matrix would hardly produce reliable results.

Line 241. It is not stated that the correlations were statistically significant at whatever level which is especially important for a small dataset. Only then one can consider strong or modest relationships based on slopes or coefficient magnitude.

Line 264. It could well be a consequence of sea sweep device generating abnormal sea spray concentrations (Na) compared to wave breaking of plunging jets/sheets reminiscent of real waves. Correlating very large numbers with very small can disturb the pattern due to the variability of each.

Line 385. What does internally mixed NaCl represent? NaCl cannot be considered separately from other sea salt ions all of which simultaneously make sea salt. Sea salt can be internally mixed with organics and if organics is primary then both are termed sea spray.

Line 396. Coagulation is extremely unlikely given very low particle numbers in clean marine air. Textbook coagulation requires many orders of magnitude higher aerosol concentrations. Sea sweep is probably different in relation to number concentration, but in any event sea sweep is poor representation of real world wave breaking produced sea spray.

Line 398. All sea spray aerosol is born as a sea water droplets. Organic matter species cannot be taken out of sea water in a dry state. Not even concentrated microlayer film can be without some amount of sea water. Therefore, it is inevitable that at least a small amount of sea salt would be present in an aerosol particle even if organic species would overwhelmingly dominate aerosol particle volume. As a consequence, primary sea spray components cannot be considered externally mixed, because they are variants of internal mixture. Only secondary components can be externally mixed, because they originate via different process (gas-to-particle conversion).

Figure 4. How can meaningful statistics be extracted having 3-5 samples in each type? Even 7 samples is barely enough. Presenting average and a range is all can be done here. September submicron samples suggest negative polysaccharide concentration - what does that mean?

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