

Interactive comment on “Seawater Analysis by Ambient Mass Spectrometry-Based Seomics and Implications on Secondary Organic Aerosol Formation” by Nicolás Zabalegui et al.

Anonymous Referee #3

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Synopsis:

This study describes the application of a new method (TM-DART-QTOF-MS) to the study of dissolved organic components of seawater. A major advantage of the approach is its relative insensitivity to salt, making desalination of the samples unnecessary. Data reduction techniques are used to distinguish and characterize the samples. Special attention is given to an attempt to distinguish surface microlayer (SML) composition from underlying water (ULW) composition. Finally, experiments are performed on a subset of the samples to test their ability to generate secondary organic aerosol in a photochemical reactor.

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Broad impressions:

This manuscript is mostly easy to read, and it describes the analytical methods applied in a high level of detail. I agree with the authors that there is great potential in the presented approach, and I appreciate their thorough characterization of the analytical method.

However, not enough attention has been given to the actual biogeochemical system being studied, both in terms of the sampling methods and the interpretation. As a result, I do not think the conclusions pertaining to the SOA-forming chemistry of the surface microlayer are supported by the work presented. I think that either the scope of the work needs to be reduced and the conclusions about actual marine chemistry cut back, or the analysis and interpretation need to be expanded significantly. I recommend the former. This analytical approach shows promise; it's a proof of concept for a strategy to distinguish seawater compositional types and their potential for reactive chemistry. But this manuscript has not shown in a compelling way what actually distinguishes SML from ULW, or SOA-forming organics from non-SOA-forming organics.

Major comment 1:

The samples were frozen upon collection without any filtration. They were then thawed for analysis and centrifuged to remove large particles and colloids. This processing will result in the lysis of intact cells present in the samples, releasing dissolved compounds that will not be removed by centrifugation and will be included in the mass spectrometric analysis. One of the main reasons to perform this analysis is to understand the reactivity of the surface microlayer, and the inclusion of chemical species that were likely not available for photochemistry in the ambient environment makes this analysis difficult to interpret in that context. That is an issue that can certainly be addressed in a future study, but at the very least it needs to be discussed in this manuscript, and unless the authors can convincingly argue otherwise, it seriously limits their ability to make claims about SML reactivity. The SML can have much higher concentrations of

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particles (e.g. cells) than bulk water, so the impact of this effect could be very large.

Major comment 2:

How can we infer that the handful of species that were identified as the best discriminants of SML vs. ULW are the species that are participating in important SML photochemistry and air-sea exchange? That is extremely speculative, even if the cell lysis issue discussed above is resolvable. Is there reason to think that boron-containing oxygenated organics are good SOA formers? Aren't there probably thousands of other potentially reactive compounds that covary with the SML-determining features that are identified here? There is a serious lack of discussion of these issues in this manuscript.

Minor comments:

It is not clear to this reviewer that it is necessary to coin the term "seaomics" in order to adequately describe the analysis presented.

Page 5, section 2.3: last sentence of first paragraph is hard to understand.

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