

Interactive comment on “A Link between the Ice Nucleation Activity of Sea Spray Aerosol and the Biogeochemistry of Seawater” by Martin J. Wolf et al.

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1 Overview

Wolf *et al.* present measurements of the ice-nucleating ability and chemical composition of aerosols generated from sub-surface and sea surface microlayer samples obtained at two locations with contrasting biogeochemistry; the highly productive Eastern Tropical North Pacific Ocean and the less productive Florida Straits. Using this data, the authors present the thesis that "jet droplets aerosolized from the subsurface waters of highly productive regions may therefore be an unrealized source of effective INPs".

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Although the dataset is rather limited in scope, I have no reason to doubt the quality of the aerosol composition and ice-nucleation measurements which, presented correctly, may be of interest to ACP readers. However, I have concerns that 1) the manuscript is missing critical information on the methods used to generate the aerosol and 2) the interpretation of the data given the approaches used to generate the aerosol is flawed. As such, my recommendation is that this manuscript should only be accepted following major revisions. Below I outline my concerns as well as more minor points that should be rectified prior to publication in ACP.

2 Major comments

1) Seawater aerosolisation - The authors have used an atomizer to generate aerosols which, given the title of the manuscript, they clearly think is representative of nascent sea spray aerosol. There are several major problems with this. Firstly, the authors need to be clear about the drawbacks of using an atomiser to simulate sea spray aerosol and how atomisation differs from the natural bubble bursting process. The size distribution of the aerosol generated by an atomizer will be very different to the size distribution of aerosols generated using both other common laboratory approaches (e.g. laminar and circular plunging jets) and, more critically, natural sea spray aerosol. The chemical composition of the aerosol generated using an atomizer is also going to be very different to the size-dependent composition of nascent sea spray aerosol e.g. O'Dowd et al., 2004 (field evidence) and Prather et al., 2013, Collins et al., 2014 etc. (laboratory evidence). Secondly, atomisation is a very energetic process during which plankton cells may be ruptured allowing ice-nucleating macro-molecules to be dispersed through the aerosol population (e.g. Ickes et al., 2020). The authors should also include some mention of this and that this will once again differentiate the aerosol they generate from that which is formed by bubble bursting at the ocean surface. Thirdly, and most critically, it is completely unacceptable to equate atomisation of sub-surface seawater

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samples with jet droplet formation by bubble bursting. As such, all reference to jet droplets in the context of the results and discussion presented by the authors needs to be removed (see relevant lines in the minor comments below).

2) With regards the aerosol generation approach used by the authors, another major issue is that the size distribution of the atomiser used by the authors is not presented anywhere in the manuscript. Indeed the authors also fail to present an adequate description of the "custom" atomiser itself. All of these major issues must be rectified prior to publication in ACP.

3) Critical literature is missing from the introduction - While the introduction is generally well written it is missing a balanced discussion of the dependence of nascent sea spray aerosol composition on seawater biogeochemistry something which is critical given the topic of the manuscript. See my detailed comments below.

3 Minor comments

Page 1, Line 31 - "Jet droplets aerosolized from the subsurface waters of highly productive regions may therefore be an unrealized source of effective INPs" should be removed since the authors have not probed jet droplets specifically.

Page 3, Line 21 - The authors do an adequate job of introducing the process of natural sea spray formation in this paragraph. However, they have not introduced the mechanism by which they generate aerosols. This would be an ideal location to contrast the two aerosol formation approaches and the properties of the aerosols that result.

Page 3, Line 27 - The authors state the following: "SSA particles produced from jet drops are composed mainly of inorganic salts but may also contain whole or fragments of cells and soluble organic molecules in subsurface waters (Wilson et al., 2015; Wolf et al., 2019). Film burst particles can contain higher mass fractions of semi-soluble

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and insoluble organic molecules in the sea surface microlayer (Cochran et al., 2017)." While the authors are right to point out the current consensus that film droplets and jet droplets likely have distinct chemical characteristics I disagree with the use of solubility as a means of distinction. I would argue that there is consensus that it is the propensity of a molecule to go to the air-sea interface, that is surface-activity, that likely distinguishes which molecules are more likely to be present in the film droplets than the jet droplets and that solubility \neq surface-activity when considering the plethora of organic compounds present in seawater. Two very similar compounds with equal surface-activity, both of which reduce interfacial free energy, can differ greatly in their behaviour because of a different degree of bulk solubility. Given this I would suggest the authors amend this statement.

Page 3, Line 31 - The authors state that "The biogeochemistry of seawater can have a large impact on the composition of SSA". This is a generalisation that needs to be expanded upon with reference to the literature. The degree to which the composition of primary sea spray is affected by biological activity in the surface ocean is a long-standing question in the field. For example, recent field experiments where open ocean seawater were bubbled indicate that biological productivity has a minor influence on sea spray organic carbon content and composition (and its CCN properties for that matter) e.g. Bates et al., 2020; Quinn et al., 2014; Russell et al., 2010. Indeed, Beaupré et al. (2019) recently reported that highly aged DOM carbon could account for 19-40% of the organic carbon in artificially generated sea spray. In contrast, Ceburnis et al. (2016) found that most organic enrichment in marine aerosol over the southern Indian Ocean was attributable to fresh POM. This dichotomy needs to be accurately represented in the introduction to the manuscript.

Page 4, Line 6 - Since the authors state that " Measurements of INP concentration and activity from diverse marine regions are relatively rare" they should be able to provide an overview here. Given this some important recent literature is missing here (Creaman et al. 2019; McCluskey et al. 2018; Gong et al. 2020; Ickes et al. 2020).

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Page 4, Line 14 - "This indicates that jet droplets in these regions may be an overlooked source of INPs" should be removed since the authors have not probed jet droplets specifically.

Page 4, Line 33 and Figure 2 - Sampling using a glass plate is a standard method in use since the early 70's. Given this it has been used in 100's if not 1000's of studies and there is absolutely no need to dedicate a figure in the main manuscript to it. As such, I suggest the authors either completely remove figure 2 or at the very least place it in the supplementary information.

Page 4, Line 34 and Table 1 - The authors state that "rough seas precluded" collection of surface microlayer samples some distance away from the ship. Indeed table 1 shows that the average wind speed at the sampling locations was 15 m s^{-1} and 13.5 m s^{-1} in the Florida straights and the Eastern Tropical North Pacific Ocean, respectively. These are very high wind speeds for sampling surface microlayer (experience tells me this was difficult!). Given this, I think some discussion on the potential impact of such rough seas on both the formation and persistence of the surface microlayer as well as the sampling is warranted here. For example, see the discussion in Rahlff et al. (2017), Sun et al. (2018), Engel et al (2018).

Page 4, Line 37 - Although the authors have used a common approach to estimate the thickness of the sea surface microlayer they sampled, this number is highly uncertain and presenting it suggests higher confidence in it than is warranted. Given that this information is not at all critical to the later discussion I suggest the authors remove the following sentences "Based on the volume of seawater collected per dip and the surface area of the plate, the thickness of the organically-enriched layer adhering to the plate was on average $26 \mu\text{m}$. This falls within the range of previous findings (Irish et al., 2017)."

Page 5, Line 5 - The following issue is certainly not limited to this study but should be mentioned here so that the authors and future readers of this manuscript interested

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in conducting similar experiments are aware. Given the high solubility of many of the surfactants enriched at the ocean surface a subsurface sample will rapidly form its on microlayer in a sample bottle or atomiser that may be very similar to a co-located microlayer sample. For example, there is a significant body of literature presenting direct estimates of microlayer formation rates following disruption (e.g. Dragčević and Pravdić, 1981, Kozaraca et al., 2005, Kuznetsova and Lee, 2001, Van-Vleet and Williams, 1983, Williams et al., 1986, Cunliffe et al., 2013) and the current consensus is that they are rapid, typically < 1 min. This point further highlights the issue with the authors suggesting atomisation of their sub-surface samples can be equated with jet drop formation.

Page 5, Line 15 - The authors state that they use a "custom Collison-type atomizer" but do not provide any further information. Given the critical role this apparatus has to the study I would like to see either a reference to where it is described in detail or further details here. For instance, a schematic of the atomiser in the supplementary information would be much more useful than a schematic of glass plate sampling.

Page 5, Line 21 - " Particles were size selected (mobility diameter = 200 nm)..." The authors state which size of particles were investigated in terms of the chemical composition and ice-nucleating ability but the reader has no sense of what the overall particle size distribution looked like given that none is presented. If the atomiser the authors used is anything like those I have encountered previously it will produce a narrow size distribution with relatively small particles. However, this is complete speculation until the authors present the size-distribution which they must do.

Page 8, Line 14 - "Our compositional analysis demonstrates that the ocean biogeochemistry impacts the composition of SSA". Given the actual experiments conducted by the authors the language used in this sentence is far too strong. The analysis conducted by the authors demonstrates that aerosols generated by an atomiser from seawater with very different biogeochemical states have differing composition.

Page 9, Line 15 - "This indicates that both jet drop particles originating from subsurface

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water and smaller film burst particles originating from the sea surface microlayer in productive marine environments can be effective depositional INPs. These organically-enriched jet droplets can constitute a large fraction of submicrometer SSA (Wang et al., 2017)" should be removed since the authors have not probed jet droplets specifically.

Page 10, Line 12 - "Atomizing seawater creates SSA with more uniform composition than natural seawater aerosolization processes, as it does not mimic the film burst and jet drop aerosolization processes that create organically enriched and depleted SSA, respectively." Here the authors have nicely summarized the major issue with the manuscript in its current form. This discussion belongs much earlier in the manuscript alongside the introduction of the process of film and jet droplet production in natural bubble bursting (see my comments above). Also, I would like to see a reference for the statement "Atomizing seawater creates SSA with more uniform composition than natural seawater aerosolization processes...". Do the authors have evidence for this or is it simply speculation? It is critical when it comes to the next point.

Page 10, Line 16 - "Our derived ns values may therefore be lower estimates for immersion mode INP activity." Following on from my previous point, given that the authors provide no evidence suggesting that atomized seawater has a more "uniform composition than natural seawater aerosolisation processes" this sentence is idle speculation and should be removed. It would be equally unjustified for me to say that the narrow size distribution with small particles that are likely more enriched in organic material compared to larger particles sizes will bias estimated ice nucleation site densities to higher values compared to natural aerosol. Without further information we cannot say either way.

Page 10, Line 34 - "Both film burst and jet droplet particles generated from microlayer and subsurface waters in productive regions such as the ETNP are likely to be sources of effective INPs. In less productive regions, film burst particles may be the dominant source of marine INPs." This statement may well be true but the authors have not generated data that would allow them to test this so both these sentences must be

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removed.

Page 11, Line 12 - "The subsurface is aerosolized through bubble bursting mechanism, which create jet droplets (Pruppacher and Klett 1980, Wilson et al. 2015, Wang et al. 2017). This implies that jet droplet aerosols generated in coastal upwelling regions or during spring phytoplankton blooms can be a source of INPs." Again, the authors have not generated data that would allow them to test this so both these sentences must be removed.

Page 11, Line 34 - "However, our results demonstrate that larger jet drop particles originating from highly productive subsurface waters may be a source of effective INPs as well." Again, the authors have not generated data that would allow them to test this so both these sentences must be removed.

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