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Atmospheric Chemistry and Physics
Discussions

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.

Anonymous Referee #1

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Review of "A Link between the Ice Nucleation Activity of Sea Spray Aerosol and the Biogeochemistry of Seawater." by Wolf et al., submitted to ACPD

The study examines laboratory generated particles from samples of seawater and the surface microlayer from two different locations wrt. their ice nucleation ability. It is an interesting study, showing that oceanic productivity and ice nucleation ability of the related particles are somewhat connected. It is suggested that jet droplets occurring during sea spray production might play a larger role for atmospheric INP, which, however, is not really examined in the study itself, as all examined particles are generated artificially and the sea spray particle generation mechanism was not examined at all.

While the topic of the paper is interesting, writing needs to be improved in a number of locations. Particularly the introduction needs to be improved a lot. It does not really focus on marine INP (which it should have), but instead is a broad collection of information given in detail which would not need to be so detailed (such as different types of INP or mixed phase and cirrus clouds). This contrasts with the fact that publications dealing with topics related to the content of this manuscript are missing. The focus of this introduction does not fit to the scope of the manuscript. Comments on the "Introduction"-section are therefore given separately below.

Another more general concern is the use of the word SSA (sea spray aerosol) for the particles examined here. SSA is a specific aerosol generated by wave activity and bubble bursting - and then an aerosol always includes particles as well as the gas-phase around them. Strictly speaking, the study examines particles generated from sea water samples. To avoid confusion, I would recommend using SWP (sea water particles) or such. Also, it needs to be check throughout the text if it is referred to particles or really all of the aerosol. Generally, the use of "P" (particle) instead of "A" (aerosol) will be better.

Once these issues, together with the other more detailed ones below will have been addressed, the manuscript can be considered for publication in ACP. But a thorough revision of the manuscript is needed at first.

Introduction:

p2, lines 8-11: These two sentences (starting with "Ice formation" and ending with "important") don't make sense together. Ice-formation (meaning the mechanism of ice nucleation) is NOT the Wegener-Bergeron-Findeisen effect. The latter concerns growth of ice crystals even in regions that have relative humidities < 100% wrt. liquid water. These sentences need to be completely reformulated.

p2, line 17: Citing Whale et al. (2018) for this is awkward as this is textbook knowledge.

p2, lines 17-30: The different heterogeneous ice nucleation mechanisms are not clearly described, and their importance is not mentioned (immersion freezing is thought to be the most important for mixed phase clouds, for cirrus this is not clear yet). Instead, remarks are made on comparably unimportant effects. This needs to be rewritten.

p2, line 20: "pore condensation and freezing" was first suggested and examined in Marcolli (2014), so it would be fair to cite that publication here. Or to skip that mentioning completely, as this is not what you are looking at.

p2, lines 33-37: There is no need to go into so much detail for types of INP which are certainly NOT emitted by the ocean. It is also somewhat unclear which citation here is given for which type of INP. Also, there are good reviews which you could cite instead, two of which you already used above (Hoose & Möhler 2012; Murray et al., 2012), but also a much older one (Szyrmer and Zawadzki, 1997) and a newer one (Kanji et al., 2017) - it would be better to cite reviews here instead of your selection, which often does not include the oldest / newest / most cited publication for the separate INP types, anyway, and which is too detailed, given your focus on marine INP.

p3, line 1: You miss all the new work on that, which should not have happened, given that this is the topic you are focusing on in here. It's weird that here now you cite review papers, on the topic you want to look at in depth. Just a selection: Burrows et al. (2013), Creamean et al. (2019), Gong et al. (2020), Ladino et al. (2019), McCluskey et al. (2018a,b).

p3, line 8: Also the link from the ocean to the atmosphere is important for your claim, and that is understudies, too! Particularly three recent publications (already included above) might be important in this respect, as they are dealing with marine INP (which necessarily includes sea spray): McCluskey et al. (2018a,b) find low INP concentrations in remote marine regions (Southern Ocean and North East Atlantic), Gong et al. (2020) find that marine INP contribute only a very small fraction of atmospheric INP in Cape Verde. As these publications are directly linked to your topic they should be dis-

cussed in your work. Also the above mentioned publication by Creamean et al. (2019) might be of interest in that respect.

p3, line 9: "DeMott et al. (2015)": I guess you mean the one that is given as "(2015b)" in your references? But that actually is "(2016)", anyway. (The preprint came out shortly before new years in 2015, but the final printing date was in 2016).

p3, lines 14-16: Is the content of this sentence related to Wilson et al. (2015) (which you cite in the beginning of the sentence before) or to Knopf et al. (2011) (which you cite at the end of the next sentence)? Clarify!

p3, line 21: "SSA encompasses a range of particle chemistries": SSA does not "encompass" particle chemistries. The chemistry goes on in the SML or sea water. Reformulate! Or if you want to point to the next sentence, then it would be "The formation of SSA encompasses a range of physical processes that affect / are affected ... ."

General comments:

p5, line 15: Give more information on the working principle of the atomizer. Your readers need to know how the particles were generated. The generation process is a big part of atmospheric SSA, in terms of particle sizes, particle concentrations and particle composition, and this is not easily reproduced with just generating particles from sea water or SML samples. You can check for some information on this issue in the introduction of Fuentes et al. (2010). "Real-world-line" SSA likely is best obtained by using wave channels (Prather et al., 2013). The generation technique you use is rather just a means to generate particles, but if they are similar to atmospheric particles generated from sea spray is a separate issue.

p5, line 21: Choosing a mobility diameter of 200nm implies that you assume that marine INP are all separately floating (likely biogenic) macromolecules. Mention that explicitly, and elaborate on that - that is one thing that could also be discussed already in the introduction. You need to justify why you can assume that this choice will not cause you to lose the majority of all INP (see Wilson et al. (2015) and Irish et al. (2017), which you already cite).

p5, lines 22-24: Doubly and triply changed 200nm particles should still be smaller than 500nm, so the choice of your cut-off might not have been optimal. You can still argue that this will remove the more highly charged particles (which, however, do not occur in such high amounts). Please check this, and also correct the text accordingly, so that others will not copy this (wrong) approach in the future. An estimation on the influence of multiply charged particles on the final results is needed.

p7, line 6: This was mentioned above, but again (and valid for the whole text): The use of "SSA" for artificially generated aerosol is a bit misleading.

p7, lines 19-26: Check this whole paragraph, together with Fig. 4. There are inconsistencies! I think that the following could remove these issues, but please check carefully for yourself: (a) line 21 -> change 4d to 4a! (b) line 25 -> change 4a to 4d! (c) "This suggests that subsurface waters in the ETNP supported more primary production." - I assume you mean compared to the Florida Straits? Then please say so explicitly!

p7, lines 28-29: Comparing averages here might seem the wrong choice, as the higher values for ETNP come from two outliers (at least to some extent). However, also if you gave the median values, your statement would still be correct (as far as I can see). Therefore, it might be worth adding the median values as well.

p8, lines 5-6: "PALMS 5 detecting ionization of more soluble organic nitrogen species in addition to amino acids." - And you assume that one would be present in higher concentration in the subsurface, the other one more in the microlayer water? Clarify! Also: Which type of detection was used by Zäncker (previous sentence)? And are you aware of the following publications: Kuznetsova & Lee (2002), Kuznetsova et al. (2004), Reinthaler et al. (2008) and Engel & Galgani (2016), who all found amino acids enriched in the surface microlayer in different oceanic regions. This may support your hypothesis, that the ionization efficiency of different compounds in PALMS might influ-

ence your results, which, however, then would have an influence on the interpretation of your data. Enrichment in the surface microlayer is not my main expertise, so take this merely as a suggestion for something you could look into.

p8, line 15: "similar and elevated organic contents" - well, this is not true for the microlayer, which has quite similar values for ETNP and Florida Straits. Only the subsurface value is higher for ETNP than for Florida Straits.

p8, lines 17-18: This last sentence of this paragraph might not be true for INP. As we don't know what it is that makes the INP, this conclusion cannot be drawn! Remove!

p9, lines 5-7: Zeppenfeld et al. (2019) finds a connection between glucose and INP concentrations in sea water samples, for real world measurements on Arctic samples. Please add.

p9, lines 17-18: I am not sure if all readers will be familiar with the study by Wang et al. (2017) which you relate to here. As this is very important for this paragraph and also for conclusions you make later, explicitly describe somewhere in your text (maybe in this paragraph here), that Wang et al. (2017) claims that jet droplets can make up a substantial fraction of all sea spray generated particles. It would be good to also be more specific instead of just writing "a large fraction".

p10, equation 1: This is an approximation which only works for really small fi ($\sim$ up to 0.1, as they are typically measured for example in the AIDA cloud chamber - but I guess you might have had higher fractions in SPIN). Otherwise, the full exponential has to be used!

p10, lines 32-33: Which surface area did DeMott use? (Hint: it is different from how you did it.) You should say explicitly in your study that the total marine aerosol includes a lot of other particles and that the n_s value you give here cannot simply be used for upscaling!

p11, lines 4-5: Here you can see very clearly that my earlier suggestion to use another name for the particles you look at, instead of SSA, makes sense. An aerosol cannot be an INP - a particle can be an INP. So in any case, “aerosols” in line 5 should become “particles”. Please check the whole text to see if you really refer to aerosol only where you mean the combination of particles with the surrounding air!

p11, lines 22-24: And yes, not only modeling studies show that, but also some of those publications using real world data which I suggested above. This should be added here.

p11, lines 29-30: ”. . . (McCluskey et al., 2018). This demonstrates that even highly productive marine environments are not always effective sources of INPs.” This is misleading - it depends on the interpretation of “effective”. If no (typically strong) land sources are nearby, then the marine environment is the only remaining source, and therefore it could be “effective”. Reformulate!

Specific comments:

p2, line 14: last word “from” -> should be “form” p3, line 24: “eject” -> “ejects” p3, line 28: Shouldn’t “in” be “included in” or “from”? p7, line 8: Following “signals”, add “with PALMS”. p8, line 2: “2017” -> “(2017)” p8, line 5: “(Figures 4b and 4e)” should only be “(Figure 4e”), or you should also mention ETNP in this sentence. p9, line 9: “2015” -> “(2015)” p11, line 18: “that that” - remove one of them.

Literature:

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