Author Response to RC1 for ACP manuscript EGUSPHERE-2024-2159 (Moore et al.)

Our responses to each comment are provided in blue text, with the reviewer comments in black. Line and figure numbers refer to the line numbers in the original submission, for consistency with the Reviewer comments. Quotations in red were added to the revised manuscript.

Summary

Whilst the authors state that these are "initial results" from the CHAOS study using the Scripps SOARS facility, this is somewhat of an understatement. The results are very comprehensive and will significantly contribute to knowledge of SSA and INP emission processes associated with wind driven mechanisms over marine sources. Based on the current results and the comprehensive and open approach, there is promise of much more to come and will encourage better and more careful approaches to ambient oceanic measurements of INP.

Despite a rapid expansion over the past decade in INP observations, using well-developed and characterised techniques such as the CSU Ice Spectrometer, there has been less progress in accurately quantifying INP emission fluxes from different source and how these emission mechanisms respond to a wide range of meteorological drivers. Whilst INP are now regarded as critical to fully understanding and predicting aerosol-cloud feedback processes, particularly in marine environments, discriminating them by their chemical composition and morphological characteristics in field studies within timescales relevant to these emission processes for more accurate parameterisation in current climate models is still limited and significantly more work is required here. As the authors state, their results reproduce well numerous previous laboratory and ambient observation studies in the Southern Ocean wrt ambient SSA concentrations due mainly to wind speed variation. However, this study has also emphasised the importance of inclusion of more detailed INP morphological analytics, particularly surface and volume site density (Niemand et al. 2012 and citations within), for future ambient studies, which is an additional excellent step forward and which more of the INP community should adopt.

Response: We thank the reviewer for their careful reading of the manuscript and the thoughtful comments and discussion which have improved it.

The introduction-review section is extremely comprehensive and very useful. [21,22,32] the authors do reference some observations in the Arctic [e.g. 21, 31, 32] as a suggestion, with respect to seasonal ambient measurements of INP and INP contributions due to biological the authors could refer to the long-term INP monitoring study in the Arctic by Freitas, G.P. et al., (2023) "Regionally sourced bioaerosols drive high temperature ice nucleating particles in the Arctic", Nat. Commun., 14, 5997, https://doi.org/10.1038/s41467-023-41696-7, 2023. Which similar heat labile INP measurement techniques combined with UVLIF single particle measurement techniques (MBS).

Response: Thank you for pointing out this very interesting paper, which discusses much-needed seasonal/annual INP and PBAP measurements in the Arctic. Freitas et al. 2023 concludes that terrestrially-sourced PBAP were the source of the high temperature INPs observed during the summer at Zeppelin Observatory (Svalbard). Our article focuses on the role of marine-derived

INPs, so we do not feel this reference belongs in the introduction, which includes citations of studies that identified marine-derived INPs in the Arctic.

It would be interesting for future SOARS studies to look to include single particle fluorescence spectral signature measurements. This would potentially expand the comparison of future SOARS studies with rapidly growing aerosol databases using integrated optoelectronic UVLIF and particle morphology measurements to discriminate INP by bioaerosol and non-bioaerosol classes and their sources, as in the Freitas (2023) study.

Response: A similar instrument to the MBS used in the Freitas et al. 2023 study (WIBS NEO) was used during the CHAOS campaign, although due to technical difficulties very little data was collected. During follow-up experiments in the SOARS channel, a WIBS NEO and other bioaerosol measurements (including DNA sequencing) were performed, and the results will be presented in an upcoming manuscript.

The authors also very carefully and clearly identify potential limitations wrt comparison of laboratory studies with ambient ship-borne observations of INP concentrations due to aerosol inlet sampling heights (0.5 to 20+ m) and coastal offset distance for tower measurements as well as the ongoing problem of inlet loss issues (well-known and difficult practical issues). These can significantly bias results as also clearly demonstrated here (and which the authors highlight in their conclusions) making it difficult to intercompare oceanic surface layer interfacial process generated concentrations with relevant cloud base level concentrations due to ship deployment differences in sampling approaches. This can be a particular problem for coarse mode particles, particularly for INP concentration quantification which can vary very significantly depending on the measurement technique employed and so needs to be better addressed in future studies.

Response: We agree wholeheartedly, and hope this can be addressed in future studies, particularly during the upcoming International Polar Year (2032-3033).

The sections on methodologies and measurement techniques are very comprehensive, particularly regarding the INP and chemical composition- and the AFM/3D imaging and force spectroscopy techniques and phase states. This provides confidence in the results. The overall description demonstrates an excellent integrated measurement technique approach with careful consideration of the uncertainties, which has been a limitation in some previous studies.

One common limitation in the study the authors highlight is the total number of individual particles that can be studied with traditional AFM, which the authors rely on for aspects of their analysis. To address this they employ a standard probability distribution analysis to assess statistical significance of their results via probability distribution curves using the standard Markov chain Monte Carlo method e.g. for morphological classes. Whilst this is acceptable to enable the conclusions presented here perhaps in future the authors should investigate more up to date neural net supervised and unsupervised approaches which are now being applied routinely to airborne single particle measurements generated by widely used biogenic aerosol integrated-optoelectronic-holographic spectrometers to identify specific emission mechanisms including particle breakup. This could allow for easier intercomparison of the SOARS data with ambient

real-time ambient measurements in the future to better identify and quantify those emission mechanisms that dominate in ambient environments.

Response: We appreciate the suggestion and will look into these neural net approaches for future studies.

It would be interesting and very useful for future SOARS studies to include/provide single particle UVLIF+ fluorescence spectra to add to the potential to ibtercompare their results with growing observational databases using this approach to segregate aerosol type. Perhaps therefore the authors could briefly mention the work by Freitas et al. "Regionally sourced bioaerosols drive high-temperature ice nucleating particles in the Arctic", Nat. Commun., 14, 5997, https://doi.org/10.1038/s41467-023-41696-7, 2023, (differentiation of sources as mentioned is this and similar studies can still be a significant uncertainty here due to meteorological driver initiating changes in emission vs particle lifetime) which compares INP measurement with biogenic discrimination and comparison with real-time UVLIF measurements at a remote Arctic station (albeit at a high elevation). I believe this would contribute to adding to the contextualisation of the SOARS data here and may be helpful to encourage community engagement to better integrate future databases generated by laboratory, in situ integrated ship and aircraft campaigns as well as long-term monitoring stations.

A relevant citation the authors should perhaps also include and comment on is, Freitas et al. (2022), Emission of primary bioaerosol particles from Baltic seawater, https://doi.org/10.1039/d2ea00047d, Environmental Science: Atmospheres, Volume 2, Issue 5, 2022. Their conclusions from a ship-borne and spray chamber study were limited but suggested very low bioaerosol contributions (< 0.5%). The importance of this contribution needs to be assessed and I wonder if here the concentration detection accuracy of biogenic INP can be quantified/highlighted a little more from this study?

Response: As mentioned above, follow-on experiments have and are being conducted in the SOARS channel, using some of the lessons learned from CHAOS. One set of experiments included measurements from a different UVLIF instrument to the MBS used in Freitas et al. (2023), the WIBS NEO, as well as other bioaerosol measurements (ie DNA sequencing), and those results will be reported in an upcoming publication. However, in the meantime, we have also added an additional paragraph to Sec. 3.2 (following line 424), which discusses the INP composition results from CHAOS, and compares them to both Freitas et al. (2022) and (2023). The new text is copied below:

"Concentrations of heat-labile INPs during CHAOS ranged from 3.1 x 10^{-3} to 4.3 x 10^{-2} L^{-1}, and when normalized by aerosol n500, from 4.0 x 10^{-8} to 1.2 x 10^{-6}. Heat treatments which produced increased INP concentrations over the untreated filters are excluded from these ranges, since they are not representative of the emission of biological INPs during CHAOS, but instead of post-emission modification. Samples meeting this criteria all had estimated biological INP fractions of 1, were at relatively warm temperatures (≥ -24 °C), and were predominantly collected at 9.6 m s^{-1} wind speed, in accordance with Fig. 4a-c. Both the concentrations and high biogenic fraction of these warm-temperature INPs from CHAOS are in agreement with recent INP measurements in the Arctic (Hartmann et al., 2020; Freitas et al., 2023), although Hartmann et al. (2020)

concluded marine INPs were the likely source, while Freitas et al. (2023) determined local terrestrial primary biological aerosol particles (PBAPs) were the dominant contributor to their measurements. Using a plunging jet chamber to produce SSA, Freitas et al. (2022) estimated the production of PBAPs from Baltic seawater to be ~1 in every 10^4 particles larger than 0.8 μm. This is about 3 orders of magnitude larger than the median proportion of biological INPs to total particles larger than 0.5 μm during CHAOS (~6 in every 10^7), indicating that while marine biogenic particles can act as INPs, only a small fraction are able to do so, at least for temperatures ≥ -24 °C."

An interesting conclusion from this study, is that "seawater ice nucleating entity concentrations during CHAOS were stable over time, indicating changes in atmospheric INPs were driven by wind speed and wavebreaking mechanics rather than variations in seawater chemistry or biology." Can it be better contextualized that this is specigic to the Pier sample site and perhaps state here how its variability compares to other locations with respect to changes in marine surface chemistry?

Response: We have added additional details to Sec. 3.1 (following line 406) which provides additional context for the CHAOS measurements and reiterates the need for future experiments with a variety of seawater biological and chemical conditions. The added text is copied below:

"Seawater biology and chemistry, as well as air and water temperature, were not controlled during CHAOS and were allowed to vary throughout the experiments. This resulted in variations in seawater chlorophyll *a*, total organic carbon (TOC), temperature, salinity, and nutrient concentrations, among other factors (Fig. A2). As a result of collecting seawater from the SIO pier to fill the SOARS channel, the CHAOS measurements may be more representative of mid-latitude coastal marine regions than remote or polar ocean environments. In addition, the seawater was relatively warm (~25 °C) as well as high in silicates, so additional measurements under a range of biogeochemical conditions are needed to assess the robustness of these findings."

I found the section describing higher INP concentrations seen at high wind speeds interesting and the point regarding peroxide-treated filter samples generating uniformly higher INP concentrations than untreated samples even more interesting with respect to stable organic components of oceanic emissions which has consequences for future measurement technique assessment in these environments.

Response: We also found this to be a very interesting result and hope it will receive further study.

Discussion

Purely for discussion and not required for inclusion in this work, I wonder if these results may eventually be used to potentially link to more fundamental oceanic biogeochemistry cycles? Specifically with respect to marine-reduced organic nitrogen components of the oceanic N cycle. It has recently been observed e.g. that biologically rich oceanic environments appear exhibit much larger concentrations of gas phase urea over the lower MBL than previously thought and

this may be responsible for enhanced redistribution of reduced N over seawater surfaces, although the impact on new particle formation and INP in marine environments is still being investigated. [Matthews, Emily, Bannan, Thomas J., Khan, M. Anwar H. et al. (20 more authors) (2023) Airborne observations over the North Atlantic Ocean reveal the importance of gas phase urea in the atmosphere. Proceedings of the National Academy of Sciences of the United States of America. e2218127120. ISSN 1091-6490]

Response: This is a very interesting comment, although outside the scope of this current study. During and after CHAOS, the SOARS channel has been used for measurements of air-water partitioning of gases and future plans include studying atmospheric aging of particles and new particle formation. A large oxidation chamber is attached to the SOARS channel and can help answer some of these questions once testing is completed. Additionally, studies which will include more focus on and control of seawater chemistry and biology, and the links between seawater biogeochemistry and oceanic emissions of gases and particles are planned for the future.

510 A9), which has not been previously seen for marine INPs. We hypothesize that spume droplet production at higher wind speeds, coupled with the low height of the SOARS sampling inlet, may have allowed for the sampling of larger, aggregate particles containing multiple INPs, which were broken up through peroxide digestion. The composition of INPs emitted in such gels is unknown, since results from CHAOS are consistent with dust or other inorganic contaminants that are unaffected by peroxide digestion, or heat stable organics which are only released from the larger particle and not broken down due to the 20-min

Response: This appears to be copied from the submitted manuscript, lines 510-515.

Overall, I found this study was excellently performed and the review of current knowledge in the field extremely useful. Their use of integrated INP and chemical composition/morphology measurements was excellent and serves as a useful reference for future studies. The interpretations and conclusions were also presented in an open manner with useful aims and objectives outlined for the community. I found this paper to be excellent therefore, bordering on exceptional (? although these are “preliminary results”), and easily worthy of publication in ACP. This paper will significantly contribute to enhancing scientific knowledge in this complex subject area and encouraging future, better integrated research in this field. I look forward to seeing more results from CHAOS/SOARS.

Response: Thank you, we greatly appreciate the comments and feedback.

Additional References

Pereira Freitas, G., Kopec, B., Adachi, K., Krejci, R., Heslin-Rees, D., Yttri, K. E., Hubbard, A., Welker, J. M., and Zieger, P.: Contribution of fluorescent primary biological aerosol particles to low-level Arctic cloud residuals, Atmos. Chem. Phys., 24, 5479–5494, https://doi.org/10.5194/acp-24-5479-2024, 2024.

Pereira Freitas, G., Adachi, K., Conen, F., Heslin-Rees, D., Krejci, R., Tobo, Y., Yttri, K. E., and Zieger, P.: Regionally sourced bioaerosols drive high-temperature ice nucleating particles in the Arctic, Nat. Commun., 14, 5997, https://doi.org/10.1038/s41467-023-41696-7, 2023.