<u>Response to Reviewer 1</u> on "Investigation of New Particle Formation mechanisms and aerosol processes at the Marambio Station, Antarctic Peninsula" by Quéléver et al. submitted to ACP Discussions

"The authors present a very significant work observing the prevalence of New Particle Formation (NPF) events (~ 40%) for the later 35 days of austral summer in 2018 (15 January-25 February) at the Marambio research station (64°15'S–56°38'W), located North of the Polar region of Antarctic Peninsula, which has minimal anthropogenic influences. This manuscript characterizes NPF events, formation pathways leading to NPF, and growth parameters from reported observations of both neutral (iodic acid (IA), sulfuric acid (SA) and methane sulfonic acid (MSA)) and charged (anion clusters of dimethylamine (DMA)-bisulphate (2SA) as well as numerous ammonium-(bi)sulfate clusters) aerosol precursor molecules with their, number concentrations and size distributions. The role of abundant biogenic precursors (MSA) to aerosol formation via ocean-ice-land interactions in NPF events enhanced by optimal meteorology in austral summer for the northern Antarctic Marambio site is highlighted as well. Various insights were confirmed with past observations and some novel insights (qualitative, if not quantitative yet) were made regarding NPF pathways in Antarctic region: SA-MSA found to be more significant contributor in NPF event days compared to IA (low concentrations in this location and austral summer study period), and SA-DMA clusters being 1000x more efficient than SA-NH_3 clusters in creating peak nucleation events. However, DMA or amine concentrations are not quantified in this study to assess the exact contribution of DMA or NH_3 or amine concentrations on nucleation. Ion-induced nucleation driven by the ternary system SA-ammonia(-water) is consistent with previous observations reported in literature, but not as significant as that driven by neutral clusters. Caveats like, instrumental artifacts (not sufficiently explaining compositional factors contributing to ion-induced nucleation) and possibility that IA may contribute to NPF in other season(s). These new insights on formation of atmospheric aerosol particles are a crucial step to improve modelling capabilities in predicting the future climate in Earth system/Global-scale climate models. However, as authors suggest mechanisms need to be characterized in more detail as observed in this Antarctic polar region study. Overall, the discussions and conclusions are logically summarized, with effective visualization to present and explain the observational data in this manuscript. I would suggest the following minor and technical comments to be addressed before accepting this manuscript"

We thank the reviewer for the positive feedback and the input that are significantly improving the quality of the manuscript. We assess here the comments points by points and address the changes in the manuscript as tracked changes on Starting with highlighted comments as RC1 (as RC2 and RC3 is addresses the second and third reviewers' comment).

Minor and technical comments (C):

- **C1: Lines 15-18, Page 1:** *"Antarctic primary particles, mainly originating from sea spray or blowing snow, only weakly contribute to total particle number concentration (Lachlan-Cope et al., 2020). Secondary formation of aerosol particles, on the other hand, is believed to be the principal contributor to cloud condensation nuclei (CCN) (Jokinen et al., 2018; Kerminen et al., 2018)."* **Can the authors also quantify the above stated contributions?**

  The modelling study presented by (Merikanto et al., 2009) reports ground level total particle concentration originating from nucleation ranging from 75 % to 100 % in the region of the Antarctic peninsula, which are considerable fractions comprising both NPF mechanism both within and above the boundary layer. At the scale of the Antarctic continent, the total contribution of secondary particle to the total particle number is

estimated to ~ 98 %. More recently, (Tatzelt et al., 2021) reported only small contribution of sea spray aerosols to the CCN concentration and suggested important contributions of potential secondary formed particle around the Antarctic continent. In the previously mentioned modelling study, (Merikanto et al., 2009) suggests a contribution of secondary-sourced particles to CCN of up 87 %, for CCN at 1% supersaturations for the Antarctic continent. This number falls to 69 % considering 0.2 % supersaturation levels.

Despite the mentioned numbers, the source contribution of aerosol particle in Antarctica is highly variable and depends on seasonality and regional landscape (e.g., coastal regions vs continental plateau). Due to the sparsity of in situ measurements in the southern most continent, specific quantification of these contribution is challenging.

A typical example of this is the austral summer seasonal pulse of the particle number concentrations with total concentration increased by a factor of 20 and up to 2 orders of magnitudes (Shaw, 1979; Lachlan-Cope et al., 2020). This seasonal increase of particles was found in connection with increased emissions and/or vertical transport in the warm season and can be explained by new particle formation processes (Lachlan-Cope et al., 2020; Kerminen et al., 2018). Additionally, in situ measurement reports elevated CCN concentration by 11% as a comparison between the high season and the typical Antarctic background aerosol population (Kim et al., 2017).

We want to emphasize that the aforementioned values might not reflect the aerosol population of the Peninsula that has likely a significant influence from a marine environment. Still, we added the following sentences in the manuscript: *"Modelling studies have estimated that primary particles would only contribute to ~2 % of the total particle count that the ground level in Antarctica (Merikanto et al., 2009). Secondary formation of aerosol particles, on the other hand, is believed to be the principal contributor to cloud condensation nuclei (CCN), especially in the Antarctic peninsula were models showed contributions varying from 75% up to 100 % (Jokinen et al., 2018; Kerminen et al., 2018; Merikanto et al., 2009)."*

Finally, our work investigations did not concentrate on CCN but on secondary aerosol formation mechanistic. In our introduction, we aimed at making the point that the NPF in the region has relevance for the climate as well, thus it is important to fully understand secondary aerosol formation processes. Assessing contributions for secondary aerosol to CCN on a more local scale is of great interest and should be assessed in future dedicated work.

- **C2: Line 35, Page 1:** *"At Marambio, ABOA…"*: Please expand the abbreviation of ABOA on first use and also **highlight the location of the Marambio site more clearly in Figure 8 (using a separate legend) or through a separate figure showing the geographical location of the study site.**

  We made the mistake in the writing of the station's name, ABOA was replaced by Aboa as it is not an acronym.
  We added an additional set of figures to locate the study site in the method section as Figure 1 a), b) and c).

- **C3: Lines 39-42, Page 1:** Specify that this period corresponds to 'austral summer' (i.e., summer in the southern hemisphere) here or wherever relevant in the Introduction section: *"At the Antarctic coast, oceanic DMS concentrations are the highest during December to*

January (i.e., austral summer) *with concentration that could exceed 15 nM within the upper 10 m layer of the ocean around the Peninsula compared to a yearly average of ~5 nM (Lana et al., 2011).”*
Changes were made through the introduction.

- **C4: Lines 42-44, Page 1:** Please add suitable citations here: *“DMS has two well-known oxidation products formed from gas-phase reaction with OH radicals: sulfuric acid (H_2SO_4, SA, formed via sulfur dioxide, SO_2) and methane sulfonic acid (CH_3SO_3H, MSA), which can then initiate particle formation and subsequent particle growth.”*
(Barnes et al., 2006; Mardyukov and Schreiner, 2018) were added as suitable citations

- **C5: Lines 51-53, Page 1:** *“At the Antarctic Peninsula, the Weddell Seaside – that undergoes consistent and recurrent phytoplankton bloom episodes every early spring - is a potential reservoir for iodic acid emissions, especially due to slower ice retreat during the summer and colder sea surface temperature than the Southern Ocean on the north and west-side of the peninsula.”* a) **Suggestion to authors to highlight the geographic location of, Weddell Sea and Marambio site (used frequently in this manuscript text) in Figure 8** or in a separate introductory figure, to familiarize the wider atmospheric community readers with the context of this study at the start of the manuscript. (Same comment as on **Line 35, Page 1**) b) **Please add suitable citation(s) that establishes this early spring phytoplankton bloom as a significant source of iodic acid (IA) neutral clusters critical to NPF?**
As answered in Comment 2, we added a set of figures to ease to locate the study site.
(Von Berg et al., 2020; Atkinson et al., 2012; Sipilä et al., 2016) were added as suitable citations.

- **C6: Line 17, Page 5:** Is it supposed to be $N_{Dp'}$ instead of N_{Dp} here? *“N_{Dp} is the number concentration of the pre-existing particles.”*
The correction was made; we thank the reviewer for noticing the typo.

- **C7: Line 49, Page 5:** edit to “area”: *“(especially in the Weddell Sea aera)*”
The correction was made.

- **C8: Lines 1-17, Page 8: Can the authors elucidate more on different possible reasons/hypothesis on why, formation rates for 1.5 nm and 3 nm particles** ($J_{1.5}$ and J_3) **observed in this study are much higher than those observed in past literature**? Also from **Lines 295-301, Page 18 [(7) in Discussion]** is convection (upward/downward draft) a possible explanation? And what further steps say via modelling or analysis can validate that?

Our data shows significantly higher nucleation rate for small particles than referenced in the literature. Although, measurement of the smallest particle in the range of 1-3 nm requires relatively recent measurement techniques - especially using the nCNC (PSM + CPC), it is possible than these values could be impacted by downward transport from the upper tropospheric layer as Merikanto et al. (2009) shows significant contribution of upper tropospheric nucleated particle to the total particle number in antarctica. This is why, we still mentioned it in Point (7) of the discussion. Still, the contribution from boundary layer nucleated particles to the total aerosol number is also seen particularly high in the area from the southern-most sector of South America and at the Antarctic peninsula as well.

Given the fact that we observed NPF already from very small sizes of the nCNC, it is also reasonable to conjecture rather local formation within the boundary layer as well. In this marine-influenced site, it is very likely that there would be much more source of condensing vapours (as those measured and showed in our studies, but potentially other vapours as well) and lower sinks than at the other Antarctic sites (used to compare our observed nucleation rates).

With the lack of information about atmospheric mixing we can hardly make a statement toward one explanation or another and aimed to bring both aspect in the discussion section of our paper. In the manuscript, we considered trajectory altitudes, however it was not precise enough to discuss on the transports of aerosols or their precursors from the upper troposphere to the low boundary layer level. One solution could be to implement a regional chemical transport model adapted to a 3-dimensional system. As an example, the trajectory model for Aerosol Dynamics, gas and particle phase CHEMistry and radiative transfer ADCHEM (e.g., (Roldin et al., 2011)) could be an interesting approach to understand the characteristic, however it required a good understanding of the component of the model such as the chemical characterisation of both aerosol and gas-phase (which we aimed to reach in our study). Still, the origin of many compounds remains unknown and would be rather inaccurate to feed the model, also the big uncertainty on the real quantities of gas emissions, e.g., especially, ammonia would challenge the performance of the model and would likely false its interpretation. Also, this model (as other) was built including VOC emissions and oxidation production. In our case in lack of vegetation, we were unable to as VOC initial concentration or detect HOM reliably, probably due to the absence of targeted instrumentation, on one site, and likely a lack of organic emissions, on the other side. Once again, our study really stresses the need for ammonia and ammonia measurement as well as chemical characterisation of the aerosol phase with better time resolution to fully resolve NPF at this marine/ Antarctic site.

- **C9:** **Section 3.3.1, Page 10-11:** Briefly mention how 'zenith time' differs from noon (midday), at the first use of the term.
  With Zenith time we meant solar noon which for instance is different from 12:00 if located in high latitude. E.g., on 16 February 2018 at Marambio the solar noon was at 13:01.
  We modified the text as "*...peaking radiation time close to noon-time – coinciding with local zenith time, i.e., solar noon that is slightly later than midday - ...*"

- **C10:** **Lines 79-80, Page 12:** Please use consistent time format (12:00 or 24:00 hours, also ensure it throughout the manuscript) : *"...respectively around 05:30 – 06:30 and shortly after 13:00."*
  Here by 05:30 and 06:30 we mean 5.30 am and 6:30 am. We went thought the manuscript and insured a consistent time format.

- **C11:** **Line 185, Page 15 & Line 275, Page 17:** edit typo: *pinguin* to "penguin"
  The correction was made.

- **C12:** **Figure 7:** See if it can be revised with better resolution and labels (axis labels).
  We improved the quality of the figure and changed the labels

Additional references:

Atkinson, H. M., Huang, R. J., Chance, R., Roscoe, H. K., Hughes, C., Davison, B., Schönhardt, A., Mahajan, A. S., Saiz-Lopez, A., Hoffmann, T., and Liss, P. S.: Iodine

emissions from the sea ice of the Weddell Sea, Atmos. Chem. Phys., 12, 11229-11244, 10.5194/acp-12-11229-2012, 2012.

Barnes, I., Hjorth, J., and Mihalopoulos, N.: Dimethyl Sulfide and Dimethyl Sulfoxide and Their Oxidation in the Atmosphere, Chemical Reviews, 106, 940-975, 10.1021/cr020529+, 2006.

Kerminen, V.-M., Chen, X., Vakkari, V., Petäjä, T., Kulmala, M., and Bianchi, F.: Atmospheric new particle formation and growth: review of field observations, Environmental Research Letters, 13, 103003, 10.1088/1748-9326/aadf3c, 2018.

Kim, J., Yoon, Y. J., Gim, Y., Kang, H. J., Choi, J. H., Park, K. T., and Lee, B. Y.: Seasonal variations in physical characteristics of aerosol particles at the King Sejong Station, Antarctic Peninsula, Atmos. Chem. Phys., 17, 12985-12999, 10.5194/acp-17-12985-2017, 2017.

Lachlan-Cope, T., Beddows, D. C. S., Brough, N., Jones, A. E., Harrison, R. M., Lupi, A., Yoon, Y. J., Virkkula, A., and Dall'Osto, M.: On the annual variability of Antarctic aerosol size distributions at Halley Research Station, Atmos. Chem. Phys., 20, 4461-4476, 10.5194/acp-20-4461-2020, 2020.

Mardyukov, A. and Schreiner, P. R.: Atmospherically Relevant Radicals Derived from the Oxidation of Dimethyl Sulfide, Accounts of Chemical Research, 51, 475-483, 10.1021/acs.accounts.7b00536, 2018.

Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of nucleation on global CCN, Atmos. Chem. Phys., 9, 8601-8616, 10.5194/acp-9-8601-2009, 2009.

Roldin, P., Swietlicki, E., Schurgers, G., Arneth, A., Lehtinen, K. E. J., Boy, M., and Kulmala, M.: Development and evaluation of the aerosol dynamics and gas phase chemistry model ADCHEM, Atmos. Chem. Phys., 11, 5867-5896, 10.5194/acp-11-5867-2011, 2011.

Shaw, G. E.: Considerations on the origin and properties of the Antarctic aerosol, Reviews of Geophysics, 17, 1983-1998, 10.1029/RG017i008p01983, 1979.

Sipilä, M., Sarnela, N., Jokinen, T., Henschel, H., Junninen, H., Kontkanen, J., Richters, S., Kangasluoma, J., Franchin, A., Peräkylä, O., Rissanen, M. P., Ehn, M., Vehkamäki, H., Kurten, T., Berndt, T., Petäjä, T., Worsnop, D., Ceburnis, D., Kerminen, V.-M., Kulmala, M., and O'Dowd, C.: Molecular-scale evidence of aerosol particle formation via sequential addition of HIO3, Nature, 537, 532-534, 10.1038/nature19314, 2016.

Tatzelt, C., Henning, S., Welti, A., Baccarini, A., Hartmann, M., Gysel-Beer, M., van Pinxteren, M., Modini, R. L., Schmale, J., and Stratmann, F.: Circum-Antarctic abundance and properties of CCN and INP, Atmos. Chem. Phys. Discuss., 2021, 1-35, 10.5194/acp-2021-700, 2021.

Von Berg, L., Prend, C. J., Campbell, E. C., Mazloff, M. R., Talley, L. D., and Gille, S. T.: Weddell Sea Phytoplankton Blooms Modulated by Sea Ice Variability and Polynya Formation, Geophysical Research Letters, 47, e2020GL087954, 10.1029/2020GL087954, 2020.