<u>Response to Reviewer 2</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

"Since the second referee report is still missing, I will provide a review so that the open discussion can be closed. Quéléver et al. present an extensive study on new particle formation using data derived during a measurement campaign at Marambio station in 2018. The paper is generally well written and I only have suggestions for minor revisions ".

We thank the journal for reviewing our work in the lack of referee report by the closing date of the discussion period. The constructive comments improve the readability of the manuscript and its quality. We will assess the comments points by points and address the changes in the manuscript as tracked changes on the Word document with highlighted comments as RC2 (as RC1 and RC3 are addressing the first and third reviewers' comment).

General comments:

- " For the next submission it would be good if you could use the ACP manuscript style (line spacing, font size etc. See templates on the ACP webpage: https://www.atmosphericchemistry- and-physics.net/submission.html#manuscriptcomposition). The manuscript was as it was published as preprint quite difficult to read (e.g. too small font).
- Line numbering: On the first few pages you start numbering again with each page, but the second half of the manuscript the numbering continues until the end. Should be done one or the other way, but not mixed. Also here I would suggest to check the ACP guidelines which is the correct style."

We apologize for the poor readability of the manuscript in the pre-print form. The new version of the manuscript is using the ACP manuscript style, line spacing and numbering, font size and style.

Specific comments (SC):

- SC1: "Abstract: The abstract is quite long and my impression is that you go between L36 and L41 too much into detail. I am not sure if it is really necessary to list here all the numbers. I would suggest to rather do that in the summary and shorten these lines here in the abstract."
  In this version of the abstract, we tried to give as much relevant information as we could overviewing the result of our study. We added values for Js and Growth rates as these are key values that we would ourselves look out in other references to compare with our own result. Also, those number are relatively out of usual, and we judged important to mentioned it as early as in the abstract. However, we do agree that this ended up to a rather long abstract and revised it to be more concise. The new version of the abstract reads as:

"*Understanding chemical processes leading to the formation of atmospheric aerosol particles is crucial to improve our capabilities in predicting the future climate. However, those mechanisms are still inadequately characterized, especially in polar regions. In this study, we report observations of neutral and charged aerosol precursor molecules and chemical clusters composition (qualitatively and quantitatively), as well as air ions and aerosol particle number concentrations and size distributions from the Marambio research station (64□15'S - 56□38'W), located North of the Antarctic Peninsula. We conducted measurements during the austral summer, between 15 January and 25 February 2018. The scope of this study is to characterize New Particle Formation (NPF) event parameters and connect our observations of gas phase compounds with the formation of secondary aerosols to resolve the nucleation mechanisms at the molecular scale. NPF occurred on 40 % of measurement days. All NPF* *events were observed during days with high solar radiation, mostly with above freezing temperatures and, with low relative humidity. The averaged formation rate for 3 nm particles (J_3) was 0.686 cm^{-3} s^{-1} and the average particle growth rate ($GR_{3.8\text{-}12\ nm}$) was 4.2 nm h^{-1}. Analysis of neutral aerosol precursor molecules showed measurable concentrations of iodic acid (IA), sulfuric acid (SA) and methane sulfonic acid (MSA) throughout the entire measurement period with significant increase of MSA and SA concentrations during NPF events. We highlight SA as a key contributor to NPF processes, while IA and MSA would likely only contribute to particle growth. Mechanistically, anion clusters containing ammonia/ dimethylamine (DMA) and SA were identified, suggesting significant concentration ammonia and DMA as well. Those species are likely contributing to NPF events since SA alone is not sufficient to explain observed nucleation rates. Here, we provide evidence of the marine origin of the measured chemical precursors and discuss their potential contribution to the aerosol phase."*

- **SC2:** "P3, L21: "sufficiently away from the station…….". Add here why. I assume it's to avoid that the measurements are affected by the station. Would be good to clearly state this."
  The clarification was made by adding "…to avoid interfering contamination signals in our measurements".

- **SC3**: "P5, L12: Add here "by collision and coalescence", so that it reads "are lost to pre-existing particles by collision and coalescence" to be more precise."
  Added to the manuscript

- SC4: "P5, L24: Also here I would suggest to add bit more information. How accurate is the approach by Kulmala et al. (2022)?"
  Indeed, this is an important point to think about, and it impacts all NPF studies comparing the J rate from events and non-event days. This is why, our co-authors designed a study in which the GR during non-event days is quantified (Kulmala et al. 2022 – under review). In order to quantify this, non-event days from 4 different locations representative of contrasting environments have been analysed (boreal x 2 , urban background, urban) – up to 10 years of data. The particle number size distributions of the non-event days during each location are averaged and then normalized by size, to enable observing a growing mode and thus calculate a GR. This study is currently under review. The results show in general, that there is not a huge difference between the GR acquired from event days and from non-event days for each of the locations, which makes us believe that using the same GR for events and non-event days in this study is plausible. Given that the data sets included in our current study from Marambio is rather short, we cannot apply the same approach as the aforementioned study. Another interesting observation is that the GR of particles in the size range 3 -7 nm, for example, is similar around the world regardless of the VOC sources (biogenic vs. anthropogenic), see for example Deng et al., 2020, which shows that the GR in Jungfraujoch and Beijing is similar within the uncertainty margins.

  For the purpose of this study, we compared the contribution of each of the terms to the total formation rate, for days with and without a GR measurement. We find, as shown in Fig. RC2-1 below, that regardless of the day, the GR term dominates the formation rate, and assuming the GR to be zero on event days (shaded green areas) will for sure, underestimate the particle formation rates in this size bin.

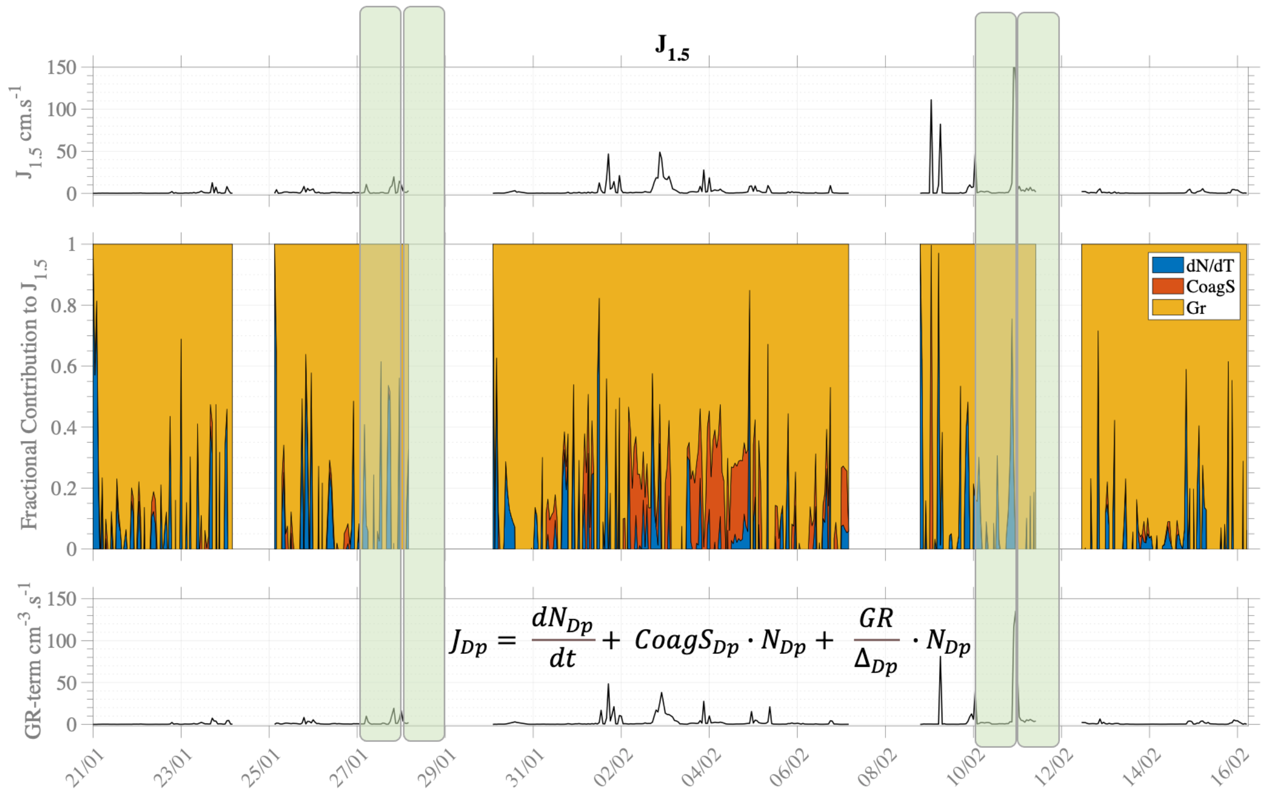

Figure RC2-1: Contribution to nucleation rate for 1.5 neutral particles. Top panel: estimated $J_{1.5}$ ($cm.s^{-1}$). Middle panel: individual contribution to $J_{1.5}$, i.e., dN_{Dp}/dt (dN/dT), $CoagS_{Dp}$ ($CoagS_{Dp} . N_{Dp}$) and Gr ($GR/\Delta_{Dp} . N_{Dp}$). Bottom panel estimated GR-term ($cm^{-3}.s^{-1}$). We highlighted un green shaded areas event days where GR could not be retrieved by measurements but with extrapolated GR.

- **SC5**: "P7, L28: Why these numbers? Why do you pick these size ranges? An explanation/justification is missing."
  A sentence was added for clarification as: *"These formation rates were calculated for the smallest possible particles but also for bigger sizes to ease the comparison with the literature."*

- **SC6:** "P8, L10-11: Sentence not clear. Please rephrase."
  The text was modified to: ***"****Although the formation rates at 1.5 nm are higher than those reported previously, the rates for larger particles (i.e., J_3, J_5, J_{10}) are comparable with the previously reported studies. This discrepancy between formations rates of 1.5 nm particles and of bigger particles could be attributed to favorable nucleation conditions (i.e., sufficient nucleating vapors) but a lack of condensable vapors contributing to particle growth which, in all, reduces the probability of particle survival."*

- **SC7:** "P13, Fig. 6 and according text: This kind of analyses is new for me and I could not follow what actually the mass defect is and would you try to extract from it. Some more motivation/explanations are required."
  We added a clarification on use of such figure and its meaning in term of chemical significance. We modified the text as: "*By showing the divergence of the exact molecular mass of a detected ion in high resolution from its integer mass (i.e., defined as mass defect), a mass defect plot illustrates the mass defect of selected ions (in y-axis) over a studied mass range (in x-axis). Compared to a typical mass spectrum this has the advantage to show the most significant ion population at once, rather independently of signal intensity which is then scaled by the marker size, easing the identification of e.g., clustering mechanisms as further discussed. There, each*

point of the mass defect plot corresponds to a unique atomic composition. An example of such representation is shown in Figure 6, for the study case of 16 February." And added *"exact mass"* in the extra explanation from Fig. 6's legend.

- **SC8:** "P14, L116: I have difficulties to follow you. To what is the "high intensity" referring to?"
  We modified the text for clarity as: *"The numerous clusters containing both sulfuric acid and ammonia, as well as the high intensity of the respective cluster signal (depicted by the marker size in Figure 6) suggest a high concentration of such ion group in the gas-phase which also could indicate an ion induced nucleation driven by the ternary system SA-ammonia(-water)"*.

- **SC9:** "P14, L133: orange dots? To which figure are you referring to? Figure 6?"
  We added the reference to Figure 6.

- **SC10**: "P14, L140: Yellow and green dots? Same here. To which figure are you referring to?"
  We added the reference to Figure 6.

- **SC11:** "P14, L143-147: Sentence not clear. Please rephrase. Maybe it's better to split this sentence into two and check the grammar."
  We rephased the paragraph for clarity as: "However, these ions were only identified as small halogen clusters of low molecular weight and with only low signal intensity. Considering previous observations in the arctic and coastal environment (Sipilä et al, 2016) only shows iodine-related nucleation as successive addition of multiple iodic acid and water group, it is unlikely that IA promotes nucleation either through neutral or ion-induced mechanism at this Antarctic site. "

- **SC12:** "P15, L162: Add "aerosols" so that it reads "sea salt aerosols"?"
  We made the modification

Technical corrections:

TC1: P2, L4: Ipcc → IPCC
TC2: P2, L5: Add a reference?
TC3: P2, L28ff: To my knowledge this are not the only references on these aerosol compositions, thus I would suggest to add "e.g." before the references.
TC4: P3, L1-10: I would suggest to add here references to the respective chapters.
TC5: P5, L49: aera → area
TC6: P7, Fig 2 caption: here "a)" etc in bold face instead of "(a)" as normal text. Be consistent and check ACP guidelines for which way of writing should be used.
TC7: P7, L23: changed → changes
TC8: P7, L25: appear → appeared
TC9: P8, L33: particle → particles
TC10: P11, L39: concentration → concentrations
TC11: P11, L42: add "is" so that it reads "that IA is even anticorrelated with….."
TC12: P11, L46: concentration → concentrations
TC13: P11, L47: concentration → concentrations
TC14: P11, 3.3.2 Header: Study case of → case study on
TC15: P13, L104: noise to signal → signal to noise
TC16: P14, L124: rate → rates
TC17: P14, L134: Add "the" → have shown the possible roles
TC18: P15, L192: Add "the" → in the Supplementary
TC19: P16, L213: concentration → concentrations
TC20: P17, L221: emission → emissions
TC21: P17, L236: study case → case study
TC22: P17, L238: pathway proceeds → pathways proceeds
TC23: P17, L240: than negative → than the negative
TC24: P17, L241: should → could
TC25: P17, L246: in CLOUD-chamber CERN → in the CLOUD-chamber CERN
TC26: P17, L247: Add "that" and use plural: indicate that very high concentrations
TC27: P18, L299: in turns → in turn
TC28: P18, L299: source → sources
TC29: P18, L308: "by key well known"? "key" obsolete?

>> All technical corrections were assessed, and the modification were done in the manuscript and commented as "RC2 >> TC#".

Additional references:

Deng, C., Fu, Y., Dada, L., Yan, C., Cai, R., Yang, D., Zhou, Y., Yin, R., Lu, Y., Li, X., Qiao, X., Fan, X., Nie, W., Kontkanen, J., Kangasluoma, J., Chu, B., Ding, A., Kerminen, V.-M., Paasonen, P., Worsnop, D. R., Bianchi, F., Liu, Y., Zheng, J., Wang, L., Kulmala, M., and Jiang, J.: Seasonal Characteristics of New Particle Formation and Growth in Urban Beijing, Environmental Science & Technology, 54, 8547-8557, 10.1021/acs.est.0c00808, 2020.

Kulmala, M.; Junninen, H.; Dada, D.; Salma, I.; Weidinger, T.; Thén, W.; Vörösmarty, M.; Komsaare, K.; Stolzenburg, D.; Cai, R.; Yan, C.; Li, X.; Deng, C.; Jiang, J.; Petäjä, T.; Nieminen, T.; Kerminen, V-M.: Quiet new particle formation in the atmosphere, Frontiers, *under review*.