<u>Response to Reviewer 3</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

"I congratulate the authors for the excellent paper, this is a ground breaking paper with lots of excellent measurements. I suggest publication on ACP following minor revisions:

1) The authors seem not to give importance to sympagic sea ice areas as a source of organic nitrogen, as discussed in Dall´Osto et al (2017), Dall´Osto et al (2019) and Rinaldi et al (2020) - given the fact it is a likely source of an important gaseous precursors, it may be worth to bring it into discussions

2) Following this, I am afraid the discussion on point 4 on page 17 is somehow hard to follow. The authors report 13 nucleation events: event 1 and 3 have high GR, event 6,9,10 have very high J. The authors then decide to reports an important case study for the last day (event 12 and 13). However, the discussion of the wind roses is rather weak. The whole interesting event of the case study event (high organic nitrogen) has the opposite wind roses of the claimed pinguin colonies. Also, event 6,7,8,9 have contrasting wind roses - so there must be some influence from the contrary sector (again coincidentally open pack sea ice regions around Marambio).

3)Following the points above, please consider to address other possible source regions. On this regards, you may want to consider to run concentration weitghted trajection for particle formation rate or to see where these particles may originate - the dataset is a brilliant one and worth analyzing a bit more in detail. Also, only one mass defect plot is presented (Figure 6). This is unusual, on previous papers (ie Antarctic measurements in Jokinen et al., 2018) mass defect api-tof measurements for each NPF events were presente - may be worth reporting them in supporting information

I congratulate once again for the brilliant dataset produced and the well presented paper, I hope these modifications can be considered before accepting the paper"

We thank Reviewer 3 for the positive review and feedbacks, and we appreciate the suggested inputs that bring more substance to the paper and significantly improve its quality. Here, we address every comment separately and make the changes in the manuscript as tracked changes on the Word document with highlighted comments as RC3 (as RC1 and RC2 is addressing the first and second reviewers' comments).

Comment 1: The authors seem not to give importance to sympagic sea ice areas as a source of organic nitrogen, as discussed in Dall´Osto et al (2017), Dall´Osto et al (2019) and Rinaldi et al (2020) - given the fact it is a likely source of an important gaseous precursors, it may be worth to bring it into discussions.

This is a very good point. Since we do not have direct measurement of nitrogen containing base species, especially nor of ammonia nor of dimethyl amine, it becomes tricky to properly assess their source. In our paper, we conjectured the penguin colony to be source of possible ammonia due to its vicinity from the measurement site. However, we cannot exclude other sources, and the sea ice could also likely explain a non-negligeable (if not the entire) fraction of nitrogen-containing species as observed from the gas-phase atmospheric composition. We now considered that aspect in the manuscript, in the result section and in the discussion section (cf. § 3.3.4 and § 4 (4)).

Comment 2: Following this, I am afraid the discussion on point 4 on page 17 is somehow hard to follow. The authors report 13 nucleation events: event 1 and 3 have high GR, event 6,9,10 have very high J. The authors then decide to report an important case study for the last day (event 12 and 13). However, the discussion of the wind roses is rather weak. The whole interesting event of the case study event (high organic nitrogen) has the opposite wind roses of the claimed pinguin colonies. Also, event

6,7,8,9 have contrasting wind roses - so there must be some influence from the contrary sector (again coincidentally open pack sea ice regions around Marambio).

We apologies the poor clarity of the discussion. We know the choosing event 12-13 as a case study is not optimum to characterize (all) NPF (occurring) at our site, especially considering the activity and elevated rates for other events. However, due to technical restrictions, we could only speculate on the possible aerosol activity to occur during the operation. Then, we had to manually stop the CI measurement and run the APi-TOF in negative or positive ion mode, inducing interruption of measurement and change on the instrument tunning. As shown in supplementary, we run the negative ion mode simultaneously to an event only 3 times during the whole campaign: on 6.2 (Event #8), on 12.2 (Event #11) and on 16.2 (Events #12-13, as our study case). We did not consider Event #8 worth of interest as (1) the growth - depicted from the shape of the size distribution was interrupted - on many occasions and (2) our ion mode measurement did not catch the start of the event and thus, would not be of use to resolve the initial nucleation formation pathway. On the other hand, Event #11 was suspected to originate from a polluted sector. In this case, we would focus our investigation on anthropogenic mechanisms rather than on the natural processes of the Antarctic peninsula. For these reasons, we decided to highlight Events #12-13 only. Joining comment 1 suggestions, we agree that the penguin-caused ammonia emission conjecture is only a possible cause and particularly in the case of Event #12-13, wind and trajectory analysis do not point toward this explanation. The activity of the sympagic environment could also very likely explain nitrogen-containing compounds although trajectory (specifically from Event #12) seems to originate from an ice-free sector (at least further away from the marginal ice zone). Still, we implemented the mentioned point (4) with this new input that actually drive the discussion to a better understanding of the role Antarctic marine ecosystem on secondary aerosol formation.

Comment 3: **Following the points above, please consider to address other possible source regions. On this regards, you may want to consider to run concentration weitghted trajection for particle formation rate or to see where these particles may originate** - the dataset is a brilliant one and worth analyzing a bit more in detail. Also, only one mass defect plot is presented (Figure 6). This is unusual, on previous papers (ie Antarctic measurements in Jokinen et al., 2018) mass defect api-tof measurements for each NPF events were present - may be worth reporting them in supporting information

In the new version of the manuscript, we now implemented sympagic water as a possible source for ammonia. We are not sure to understand what would be a '*concentration weighted trajection for particle formation rate'*, as suggested. However, we do agree that using a regional transport model, in future measurements, would be extremely useful to assess sources of aerosol and their precursors that would justify the observed high nucleation rate. Furthermore, that would help to determine if nucleation occurs locally, within the boundary layer, or in the upper troposphere, as conjectured in point (7) of the discussion. Concerning the measurement location and environment, the first step would be to get quantitative estimations of ammonia and amines, first, which we are critically missing with this dataset. Then, we should also consider additional source of ammonia such evaporation of ammonia from pre-existing (primary) particle (e.g., sea salt), also depending on particle acidity, which could be assessed in future measurement. With these considerations, additional measurement should be pursued in the future, in the same location, to properly assess all the source for the precursors that contribute to atmospheric nucleation in the regions.

The other point mentioning the one and only mass defect plot is due to the restriction in the operation of the instrument. While e.g., Jokinen et al. had two mass spectrometers, we had only one instrument to run the campaign. As mentioned in our earlier response, catching the ion composition at the start of a nucleation event requires a good prediction of the event to occurs which is not an exact science. Since we could not have simultaneous measurement of both neutral and ion composition, we had to sacrifice one measurement mode over the other in every moment. Event #12 was our best catch as wind came from favourable clean sector and the size distribution showed appearance of small clusters accompanied with continuous growth twice during the day. This, at first, allowed to describe the precursor molecules and then offered the opportunity to characterize the ion composition at the start of the second event.