We thank Reviewer #2 for his comments and suggestions which contributed to improve our manuscript. Our answers are listed below. Note that in addition to the points raised by the two reviewers, we have corrected the normalization of the amines signal in Figs. 8 and 9; in line with the actual recommendations of Simon et al. (2016), we now use the nitrate trimer signal instead of that of the dimer. This correction did not result in any change in the variability of the normalized signals, only in their amplitude, and the comparison with the observations of Brean et al. (2021) was corrected accordingly in Sect. 4.2.1:

"The C2 amine signals measured at Maïdo are <u>higher than</u> those reported by Brean et al. (2021) in the MBL (<u>i.e. closer to the ocean, which is one of the identified sources of amines</u>), <u>but they</u> show a similar diurnal cycle, with a minimum during daytime (Fig. 8.b)."

Specific:

Comment 1: Page 1 Title. The reviewer felt the title was only reflecting/summarizing part of the results presented in this study. Maybe adding the origin of air mass or clusters as well?

We have added the study of clusters' origin to the title, since it is indeed an important aspect of the analysis:

"Insights into the chemical composition <u>and origin</u> of molecular clusters present in the free troposphere over the Southern Indian Ocean: observations from the Maïdo observatory (2150 m a.s.l., Reunion Island)"

Comment 2: Page 3 Line 6. It seems a little bit contradictory to the sentences in Page 2 Line 15 where the authors cited several NPF observation in low FT or the interface of BL and FT with some of them from stationary measurements.

On Page 2 Line 15, we refer to observations in the low FT or at the interface between the BL and the FT irrespective of the terrestrial or marine environment associated with these measurements, whereas on Page 3 Line 6, we refer specifically to the marine FT, which has up to now been mainly sampled by aircraft.

Comment 3: Page 7 Section 3.1. The reviewer was wondering whether this section would fit better at the beginning of Section 2 as a separate subsection, considering it's mostly description of the measurement site from literature instead of results from this study?

This is indeed a good idea, so we have restructured Sect. 2 as follows:

<u>2.1 Observations</u>

<u>2.1.1 Atmospheric dynamics in Reunion</u>

The measurements used in the present work were performed at the high-altitude observatory of Maïdo, which is located on Reunion Island, about 15 km inland from the west coast (21.080◦ S, 55.383◦ E; 2150 m a.s.l.). Reunion Island is located in the Indian Ocean, in the descending part of the southern Hadley cell… [Current Sect. 3.1]

<u>2.1.2 Measurement site and instrumentation</u>

The data sets obtained in the framework of two campaigns conducted at Maïdo were used in particular in the present work. Data collected during the BIO-MAIDO campaign (Leriche et al., 2023; https://anr.fr/Project-ANR-18-CE01-0013, last access: April 7, 2023) between March 14 and April 8 2019 were first used… [Current Sect. 2.1]

Comment 4: Page 8 Line 9. It would be nice to add the frequency/fraction of BL thicknesses below 6m as FT conditions. Are there any periods at night that are still under BL conditions, or the station is always at FT conditions at night? Based on Fig 4 from OCTAVE campaign, it doesn't seem to be always at FT at night.

We are not sure we understood the first part of the comment. A BL thickness of less than 6m is the criterion we have chosen to identify the periods when the station lays in the FT from the model outputs. On the basis of this definition, does the Reviewer want to know the fraction of time during which the station is in the FT according to the model? If so, according to the simulations performed with Meso-NH as part of BIO-MAIDO, the station was in free troposphere 55% of the time on the 26 days considered. This frequency has been added to the text, and for consistency, the frequency of FT conditions during OCTAVE (this time derived from the analysis of σ_θ) was also added to Sect. 4.1:

- Sect. 3.1: "*In practice, for the rest of the analysis, BL thicknesses below 6 m predicted by the model were associated with FT conditions at the site* _(i.e. 55% of the time on the 26 days considered during BIO-MAIDO)_*, and the rest of the points with BL conditions.*"
- Sect. 4.1: "*Based on the analysis of σ_θ, the station was found to be 36% of the time in the FT during the 7 days of interest in OCTAVE.*"

In fact, as shown in Fig. 4, there are periods at night that are under BL conditions, which clearly demonstrates the interest of having a tracer other than an average time window for the distinction between FT and BL conditions. Nevertheless, Fig. S3 (now Fig. S4) shows that the station is mainly in the free troposphere at night (more than 80% of the time at night). These aspects are discussed in the last paragraph of Sect. 3.1.

Comment 5: Page 8 Line 15. The reviewer was wondering about the vertical wind. Would it be a better tracer to reflect the influence of BL at the site? Is the usage of horizontal wind instead of vertical wind due to the commonly-unavailability of vertical wind dataset? Could the authors clarify this a bit?

In fact, vertical wind should be a better tracer of vertical turbulence, but indeed, this variable seems to be less commonly measured than horizontal wind (it is at least not measured at Maïdo). This is now clearly mentioned in the manuscript:

"It should be noted that vertical wind is obviously expected to be a better tracer of vertical turbulence, and therefore of FT and BL conditions, but this variable is not measured at Maïdo."

Comment 6: Page 9 Line 15-16. It would be nice to provide a plot at least in SI to support the statement that the stricter threshold would not improve the results.

We are not sure to understand which type of figure is expected by the Reviewer, and we believe that the requested information is in fact already provided by Fig. 2. Indeed, in Fig. 2, we can already see that if we use a lower threshold / stricter criterion on σ_θ for the identification of FT conditions, the probability that the site is in the free troposphere is not significantly greater, unless we use a much lower threshold. For example, if the threshold on σ_θ was significantly lowered to 10°, the probability that the site is in the FT would become higher than 90%, but at the same time a higher number of FT observations would be excluded, which we want to avoid (we want to keep a balance between a sufficiently high probability of being in the FT and a criterion that on the other hand does not exclude too much FT data).

Comment 7: Page 12 Line 15-17. It seems bigger differences between the two models for Fig 3c-e compared to Fig 3b from northwest. Is there any explanation for this?

The idea here was to illustrate that the agreement between Meso-NH and ECMWF ERA-5 reanalyses concerning the estimation of the boundary layer thickness is overall much better over the ocean than over land. A detailed study of the variability of model performance over the ocean is beyond the scope of this work, and it is likely that the number of randomly selected points (4) is too limited for this anyway (a statistical approach would be needed). However, in order to answer the Reviewer's question, we have calculated, for each of the 4 selected points, the average differences between Meso-NH and ECMWF ERA-5 reanalyses. The results are as follows:

Northwest: +137 / -175 m
Northeast: +235 / -100 m
Southwest: +203 / -131 m
Southeast: +194 / -76 m

For the point located to the north-west of the island, there are more periods during which the boundary layer thickness estimated by Meso-NH is lower (and more significantly) than that derived from ECMWF; as a result, the average of the negative differences (Meso-NH - ECMWF) is logically higher overall for this point, and the average of positive differences lower overall. Beyond the amplitude of the differences, however, it would appear that the variations in BL thickness calculated by the two models are more similar for the other points.

Comment 8: Page 13 Figure 4. There are FT periods with relatively high RH values (e.g. night of April 11-12, 13-14, 14-15). Would the water mixing ratios provide better comparison for FT vs BL differences?

We thank the Reviewer for his suggestion. The water mixing ratio (WMR) does indeed show overall more pronounced contrast between the FT and the BL than RH. However, since the variations in these two variables are closely correlated (see new Fig. S8 below), the conclusions drawn from the observation of RH remain valid when considering WMR. We have nonetheless added a figure showing the timeseries of the WMR to the supplement (Fig. S8), and completed the text in Sect. 4.1 as follows:

"… although for temperature there is a bias due to the diurnal variation of the global radiation. As illustrated in Fig. S8, a more pronounced contrast between FT and BL conditions is observed when considering the water mixing ratio instead of RH (7.4 g kg^{-1} *(4.3 - 10.5* g kg^{-1}*) in the FT vs 8.6* g kg^{-1} *(4.5-11.3* g kg^{-1}*) in the BL), although the variations of these two variables logically appear to be strongly correlated. For simplicity, we have chosen to report only the analyses and results involving RH (which is measured directly) in the rest of the study, but it is worth noticing that the associated conclusions were confirmed when considering the water mixing ratio instead."*

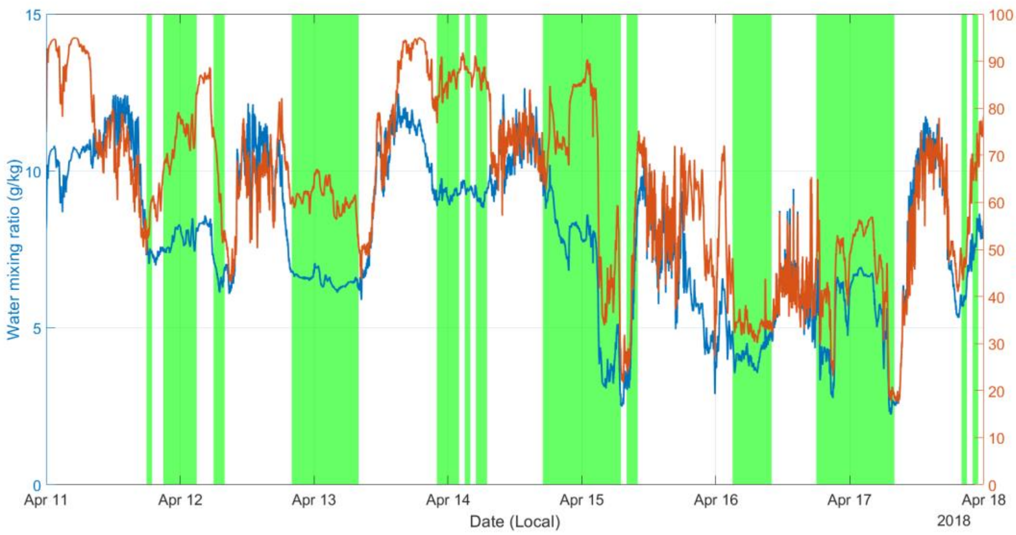

Fig. S8 Timeseries of the water mixing ratio (blue) and relative humidity (RH, orange) during the OCTAVE campaign. Green patches depict the hours when the Maïdo station is in the FT based on the analysis of the standard deviation of the horizontal wind direction.

Comment 9: Page 14 Line 13-15. Consistent with the relatively high RH values of the night of April 11-12, 13-14, 14-15 in the reviewer's previous comment, it seems these nights have air masses from pristine marine air from Indian Ocean or southern Madagascar. The reviewer would probably category Fig S6a (night of April 13-14) to group 3 like Fig 5c (night of April 14-15) instead of group 2 considering the similarity (also shown in Fig S7). Is this because it's the night with air masses passing through terrestrial boundary layer other than Reunion as mentioned in Line 27-28? Could the authors clarify this a bit?

The situation observed on the night of the 13th to the 14th can be considered as a sort of intermediary/mixture between the situations illustrated in Figs. 5.b (group 2) and 5.c (group 3); the reason why we decided to associate this night with group 2 rather than group 3 is that some of the air masses sampled during that night flew over Madagascar, which is not the case for the air masses in group c, which remain over the ocean. This classification remains indicative, however, and is only intended to provide a synthetic illustration of the different situations encountered (with respect to horizontal spatial distribution of air mass back trajectories) during the period of interest; the classes defined in Fig. 5 are not used in the rest of the analysis.

Comment 10: Page 15 Line 17-21. Considering the much higher signals of reagent ions and isotopes have been excluded from the calculation of the total signal, what's the unidentified species (>75% fractions) over the mass range 80-400Th? The fraction seems a bit high. Are they mostly organics? They are labeled as "Others" in Fig 7a with pretty high signals. More description and discussion on this are needed.

There is indeed a significant fraction of the signal measured by the CI-APi-TOF that has not been identified in this work. In response to the questions from the two Reviewers about these compounds, we have added a paragraph at the end of Sect. 4.2.1 which provides some additional elements:

"*As illustrated in Figs. 6 and 7 and mentioned above, a significant part of the signal measured with the CI-APi-TOF has not been identified, of which a certain fraction may be made up of organic compounds, and given their mass range in particular highly oxygenated molecules (HOMs). An attempt to identify the compounds observed in Hyytiälä, the birthplace of HOM studies located in the boreal forest (Ehn et al., 2012; 2014), was however unsuccessful. In particular, the molecules that were used as fingerprint for the study of HOM sources by Yan et al. (2016), are not detected at Maïdo (see Table S1 in the Supplement for a list of these compounds). A first explanation for the absence of these HOMs at Maïdo is certainly linked to the fact that their precursors, monoterpenes, are present at low concentrations, below instrumental detection limits during the night (Rocco et al., 2020). Additionally, the meteorological conditions (mainly temperature and relative humidity) and oxidant concentrations, which all certainly affect the chemical reactivity, are very different at Maïdo compared to Hyytiälä. Figure 6 also highlights a certain number of peaks associated with high signals which have not been identified, in particular at UMR 114, 134, 177, 197, 246, 260, 310, 334 and 362 Th. Since these compounds do not seem to be enriched in the FT (Fig. 6.b), they have not been the subject of in-depth study, but the time series of their signals are nonetheless shown in Fig. S14. The signals associated with UMR 114, 134, 177 and 197 Th (Fig. S14. a) show similar variations. Given the difference of 63 Th (corresponding to HNO_3), masses 114 and 177 Th on the one hand, and 134 and 197 Th on the other, are most likely associated to the same compound, therefore explaining the similarities within each pair, and the similitude between the two pairs is certainly more broadly indicative of a common source. The other masses (UMR 246, 260, 310, 334 and 362 Th) have a different behaviour (Fig. S14.b), which is actually comparable to that observed for the peaks attributed to C4 amines (Figs. 8 and 9). These observations may be the subject of more in-depth investigations in future studies dedicated to the BL composition.*"

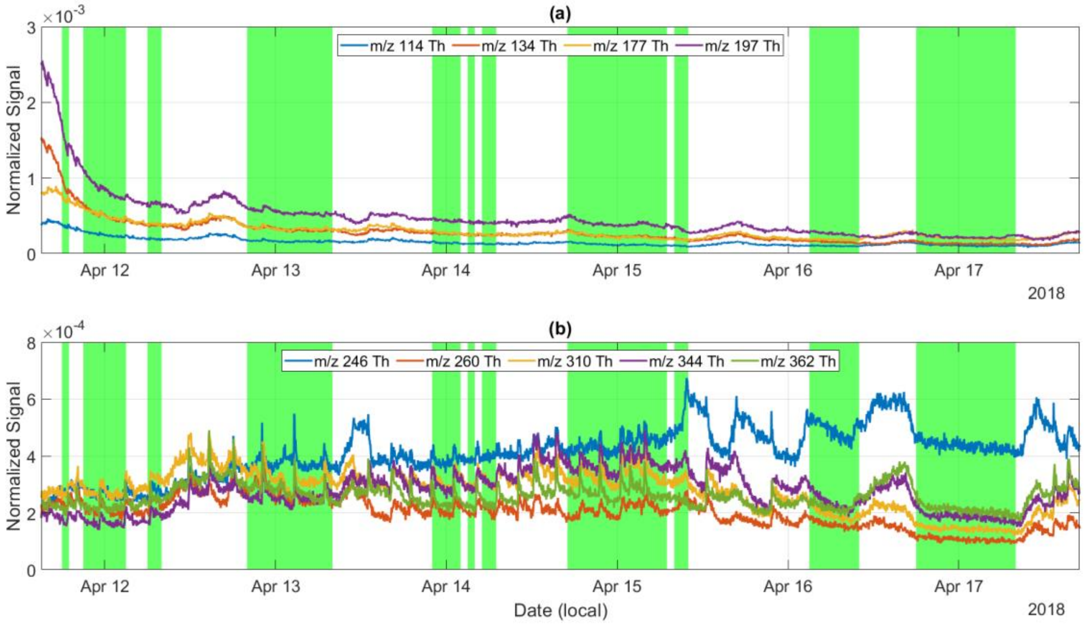

Figure S14 Timeseries of the normalized signals of UMR a. 114, 134, 177 and 197 Th and b. 246, 260, 310, 344 and 362 Th. Green patches depict the hours when the Maïdo station is in the FT based on the analysis of the standard deviation of the horizontal wind direction.

Comment 11: Page 18 Line 18-21. -Could the coinciding drop of RH be related to the advection of air masses from the higher altitude of the station? Can the models help to explain this?

As shown in the analysis at the end of Sect. 3.3 (Fig. S4, now Fig. S5), the majority of air masses reaching the site in FT conditions come from higher altitudes. In the absence of fine-scale simulations (performed with Meso-CAT) during OCTAVE, it is difficult to link RH drops to any particular behaviour of the air masses sampled at that time. We did, however, analyse the altitude of the air masses sampled when the site was in the FT during the night of the 14th to the 15th, based on the information provided by CAT (Fig. R1). While the altitudes of the air masses sampled between 7 and 9 p.m. were close to the site's altitude during the last 15-20 hours of flight before reaching the station, the altitudes were generally higher for the air masses sampled during the following hours, but without any apparent particularity for the time during which the RH drop was observed.

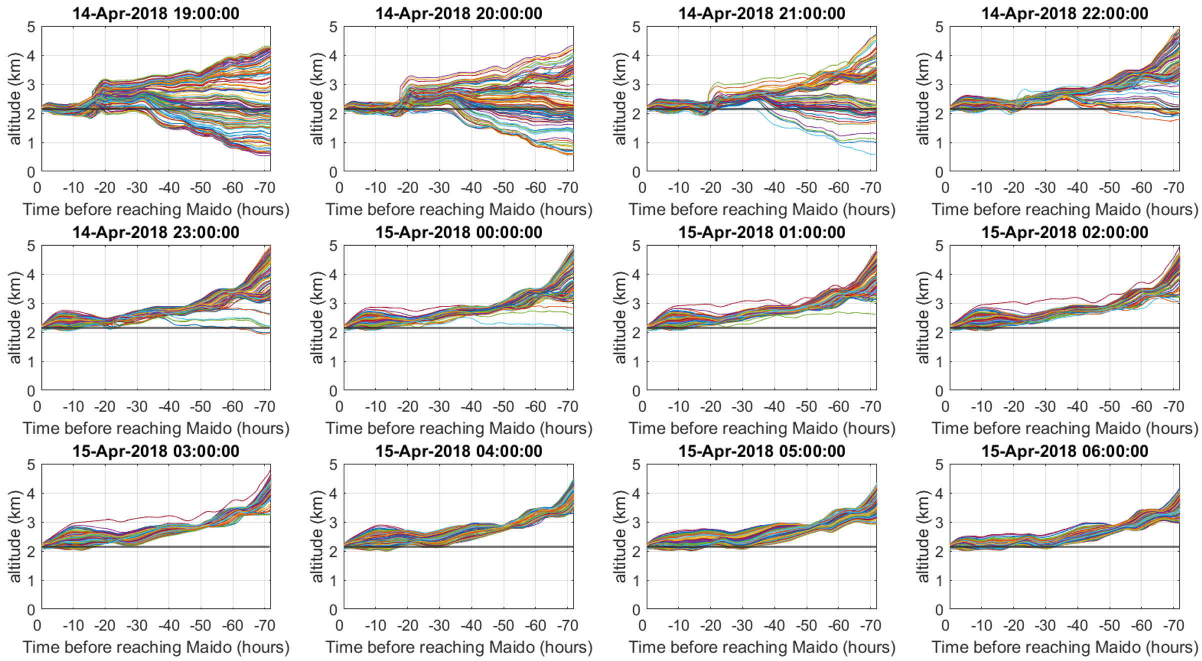

Fig. R1 Flying altitudes of air masses sampled at Maïdo during the hours when the site was in the FT during the night of April 14-15. Note that for each back-trajectory computed with the CAT model, all 125 trajectories of the corresponding set are shown in the figure.

Comment 12: Could the increase of SA be due to similar reason as the increase of MSA, i.e., the evaporation from condensed phase (Page 19 Line 26)?

We do not disagree with the possibility that evaporation from the condensed phase, possibly from evaporating cloud droplets, could be a potential source of gas-phase sulfuric acid. However, to the best of our knowledge, there is no literature that explains the underlying process. We do want to note that sulfuric acid is much less volatile than MSA, and consequently has much lower evaporation rates from gas-phase clusters than MSA (Rasmussen et al., 2022). This leads us to believe that the processes involved in the evaporation from the condensed phase of MSA and sulfuric acid are different. However, given that our work is primarily a measurement report, elucidating the actual underlying processes is beyond its scope. Nevertheless, in addition to the study of Frege et al. (2017) which we already mention, we have added a reference to the paper by Mauldin III et al. (1999), which also reports a connection between low RH and higher gas-phase sulfuric acid, and we now mention as well the work of Tsagkogeorgas et al. (2017), which would support the hypothesis of sulfuric acid evaporation from the condensed phase:

"Similar observations were reported by Frege et al. (2017) at the high altitude station of Jungfraujoch (3454 m a.s.l., Switzerland) and Mauldin III et al. (1999) from airborne measurements over the Pacific Ocean. Based on the work of Tsagkogeorgas et al. (2017), the connection between increased sulfuric acid concentration and lower RH might be explained by the evaporation of sulfuric acid from the condensed phase, which they report as the main driver of sulfur particle shrinkage at low RH combining chamber experiments and model simulations."

Comment 13: Page 20 Line 15. The reviewer was wondering how could MSA fragmentation in the mass spectrometer form SO5-? Could the authors add a reference to support?

We did not formulate this hypothesis with the knowledge of any results that might support it in the literature, but on the basis of our observations which highlight a strong similarity in the signal variations of these two compounds. We have slightly modified the wording of the sentence to make this clearer:

"Finally, <u>given the very high correlation observed between the signals of the MSA and SO_5^- groups</u>, we cannot rule out the possibility that SO_5^- is a fragment of MSA in the mass spectra."

Comment 14: Page 25 Line 10-11. The reviewer was wondering why would lower time spent over the ocean lead to higher wind speed along the air mass path. Could the authors clarify a bit and add a reference to support?

This explanation was only an assumption based on the correlations we observe between the signals of SO_5^- and MSA and the time spent by the air mass over the ocean since it last flew over land. Since we have no strong argument or reference to support it, however, we have removed this part of the discussion from the revised version of the manuscript.

Comment 15: Figure 8. Considering April 16 early morning till 10 a.m. local time was in FT conditions with not too low radiation (Fig 4), the reviewer was curious whether this day was a NPF event day since SA and MSA levels were not low? If yes, is it possible to study e.g. few hours of FT nucleation/clustering process?

Based on the measurements performed with a Neutral Cluster and Air Ion Spectrometer (NAIS; Manninen et al., 2016), there is no clear evidence of NPF on that day (that would rather be classified as "Undefined" following the usual classifications; Fig. S7), which, as a reminder (see P13, L16-17), was characterized by unusual conditions likely linked to the arrival of tropical storm Fakir, which hit the island on the 19th. This information has been added to Sect. 4.1:

"… an exception is observed on the morning of April 16, 2018 when FT conditions remain later at the station until 06:00 UTC (10:00 local time). One should note, however, that although daytime FT conditions could be sampled on that day, it unfortunately did not give the opportunity to study a case of MFT NPF as we could not identify clear evidence of NPF (this day was rather classified as "Undefined" based on the classification of Hirsikko et al. (2007); Fig. S7)."

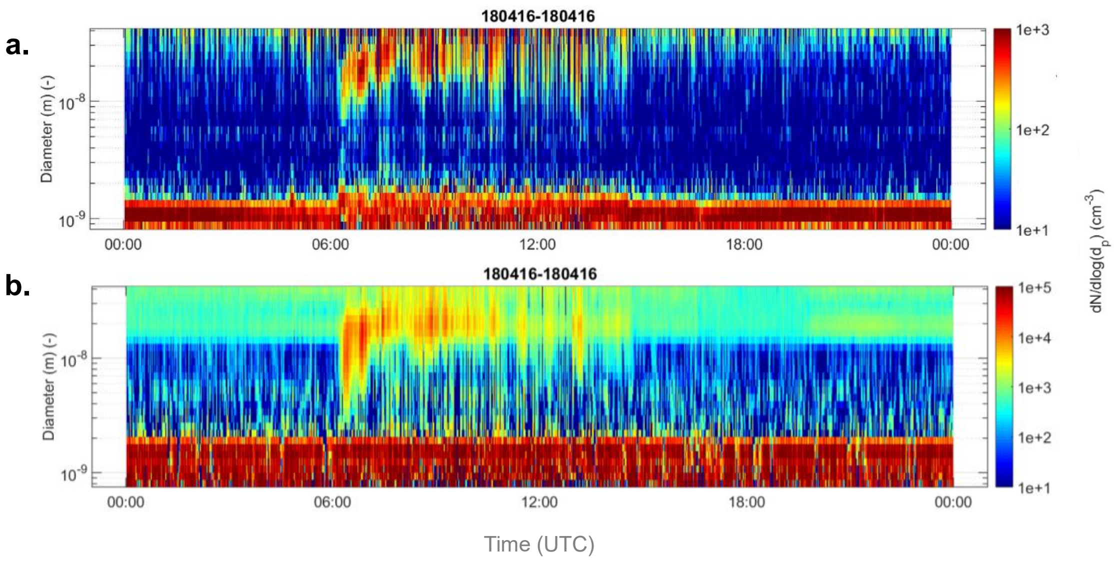

Fig. S7: Diurnal variation of a. negative ion and b. particle number size distribution measured with a NAIS on April 16th, 2018.

Technical:

Page 7 Line 7-8. Change to "the intensity of which vary…"

Done.

Page 7 Line 9. Change to "to a large extent".

Done.

Page 18 Line 2 and 14. Remove "the order of".

Ok, removed.

Page 18 Line 16. It only seems to be up to ~50% in Fig 7 on April 12. Please double check.

In fact the fraction shown in Fig. 7 for the sulfuric acid group does not exceed ~50% on April 12. The difference with the value reported in the text is explained by the fact that, as indicated on P15 L22-23, the results shown in Fig. 7 are averaged over 30 minutes to improve the clarity of the figure, while the values reported in the text were calculated on the 3-minutes averaged signals to retain the information associated with this higher temporal resolution.

Page 21 Line 15. Remove the duplicated "in".

Ok, removed.

Fig S4. It would be nice to swap the x axis from -12h on the left to 0h on the right side.

As suggested, the x-axis was swapped from -12h on the left to 0h on the right side.

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