Comments Referee #1

This study details the composition of positive and negative ions detected at Jungfraujoch over a 9 month campaign. Negative ions were primarily sulfuric acid (and its clusters), MSA, malonic, nitric, SO5- , and halogenated species. Positive ions were amines and clusters with ammonium/amines. The authors show very interesting correlations of the SO5 - and MSA, even during night time measurements. The halogenated compounds were tracked back to air masses from the ocean or sea.

This paper is written very clearly and presents new and important science about the composition atmospheric ions and the dynamics at Jungfraujoch. I recommend this paper be accepted after the authors address a few, mostly minor comments.

***Major Comments**:*

Section 3.4, NPF events: The authors explain how the mass spectra differ between observed NPF events. These results, and using FLEXPART to relate NPF to CO, have already been explained in Bianchi et al. (2016). The section in this paper does not add any more information to the results shown in Bianchi et al. (2016) and does not relate to the title/focus of this manuscript. The authors should either add in new NPF information in this section that is not covered in Bianchi et al. (2016) or should just remove the entire section (and corresponding figures and text in abstract and conclusion).

We do agree that the methods to explain NPF, FLEXPART, have already been explained in Bianchi et al. (2016), which is consistent considering that the data base for both manuscripts is the same. However, we believe that the section adds valuable information about NPF and the ion composition during NPF events. The average of many NPF events in Fig. 10 provides a robust result of the characteristic mass spectra of each type of event, reinforcing the results provided by Bianchi et al. (2016) where the authors focus on representative events (one of each type). Also in Fig. 11 we show for first time a remarkable comparison between ambient and experimental measurements (CLOUD chamber) with ion clusters up to m/z 1100. Since the results in this section correspond to the ion composition during NPF events, we believe it would be a loss of important results to remove the entire section and corresponding figures.

Page 3, Line 2 and Page 11 line 24: The authors conclude that an increase in sulfuric acid signal during the night could be due to heating of snowflakes on the APi-ToF sample tube. 1) Can the authors specify the temperature at the inlet of the APi-ToF (right before the ions enter the vacuum chamber)? Is this temperature close to the outdoor temperature or the temperature of the room the instrument resides in? Noting the room temperature would also be useful. 2) Page 8, Line 3: Is it possible that I - (or other ions) signals showing peaks at night is also due to evaporation from particles?

The temperature at the APi-TOF inlet is close to the room temperature, which would be around 15°C while the outdoor temperature would range between -20 to 10°C.

It is possible that I- and other iodine-containing ions/clusters could be enhanced due to evaporation from the particles at higher temperatures or lower humidity. However we do not observe a clear dependence of the signal on relative humidity or temperature as it was the case with sulfuric (Figure R1). Thus, there is no clear indication of a similar process. In the case of sulfuric acid, the unusual increase during night time was related to specific events of low RH or snow fall.

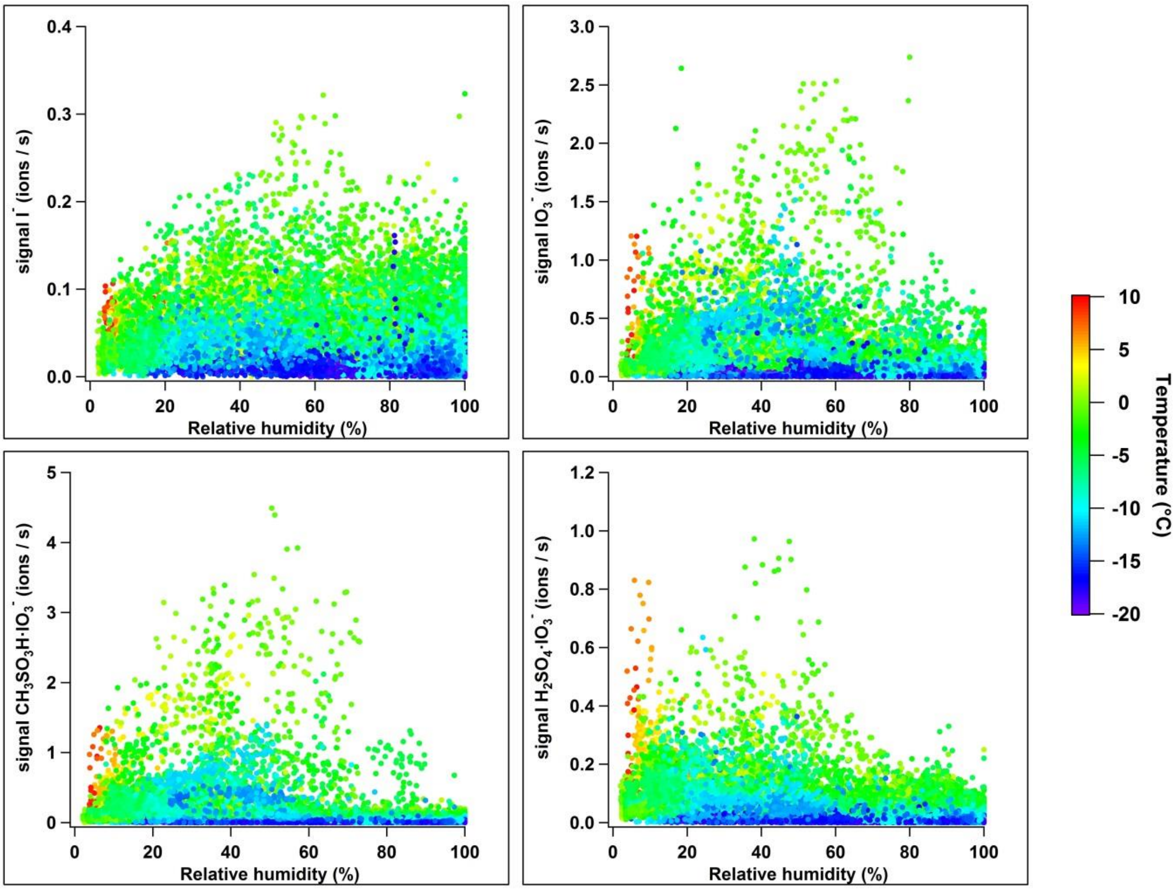

Figure R1. Signal of I^-, IO_3^-, $CH_3SO_3H{\cdot}IO_3^-$ and $H_2SO_4 {\cdot}IO_3^-$ against relative humidity and as a function of temperature. No clear dependence of the signal on relative humidity or temperature is observed as it was the case with sulfuric.

Minor comments:

Page 1, Line 20: "we also measured…" what do the authors mean by events?

We understand that the word "event" could generate some confusion since we also used it for referring to NPF. In this case we refer to occasions when the signal of sulfuric acid was higher than expected for night time conditions. We change the sentence by: "On many occasions we also saw a high signal of sulfuric acid during night time when clusters up to the tetramer were observed".

Page 1, Line 14 and Page 3, line 5: There are two altitudes listed: 3450 and 3454 m a.s.l. Page 4, line 1 gives 3454. Page 2, line 29 says 3580 m a.s.l. Which one is it? Is the mountain growing (this is a serious question)?

We apologize for this mistake; the altitude has been corrected in Page 1, line 14 and Page 2 line 29. The altitude of the research station is 3454 m a.s.l. However the Sphinx observatory is located at 3580m a.s.l. As explained on Page 3, line 30, initially the APi-TOF was installed at the Sphinx observatory but it was not possible to measure negative ions due to electrostatic interaction with the building, therefore we relocated the instrument to the research station (See Figure R2 below).

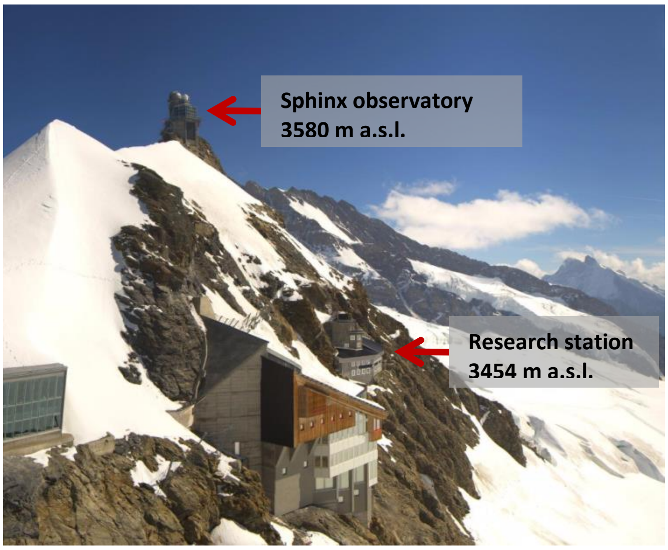

Figure R2 Picture showing the location of the Sphinx observatory and the Research station at the Jungfraujoch

Page 1, line 14: it would be useful to note the exact months and year the study was carried out instead of just saying 9 months.

This information has been added.

Page 3, Line 10: "with nine months…" not a complete sentence after the semicolon

This sentence has been rewritten as: "This work shows results from a nine-month campaign of continuous measurements with a mass spectrometer from August 2013 to April 2014 (time is shown as local standard time, UTC+1). Additionally, two intensive campaigns were conducted (January – March, 2013 and January – March, 2014) when many more instruments were employed for the study of NPF (see Bianchi et al., 2016)".

Page 5, Line 27-28: “we found mostly N-containing…” the phrase “that could not be undoubtedly” is confusing.

This phrase makes reference to the high *m/z* peaks. The precise identification of these molecules is, in some cases, not possible. These molecules could be amines or clusters of the type $C_xH_yO_z \cdot NH_4^+$ or $C_{x-2}H_{y-4}O_z \cdot C_2H_7NH^+$, having the exact same *m/z*. Making a clear distinction of cases like this is very difficult in ambient measurements.

Page 7, line 5: “sulfuric acid concentrations” The authors only use signal intensities in this paper. To use the word concentration requires showing a calibration constant of some kind. Also, it should be mentioned how the APi-ToF sensitivity would affect observed signals, i.e. are HSO4- ions transmitted/detected more efficiently than MSA ions? Without this knowledge, the reader cannot compare the signals of different ions. This explanation (or statement of the assumption the authors are using) could be added in the instrumentation description.

We agree on this point and we changed “concentrations” by “signal”. Indeed, the transmission in the APi-TOF changes depending on the *m/z* range observed, however in the Manuscript we analyzed the relative variation of the different ions to the absolute transmission. Since the tuning settings were not modified during the campaign, the transmission should not affect the relative change of individual peaks (see also Heinritzi et al., 2016). In the example that the Referee mentions, the difference in *m/z* between MSA and HSO_4^- is less than 2 Th. We do not except that the transmission efficiency will be affected in this *m/z* range. We also add a sentence in section 2.2 (Instrumentation): “For the mentioned *m/z* range it is assumed that the ions are within the detectable range of the APi-TOF and the relative change in signal of the individual ions correspond to the absolute transmission”.

Page 8, Line 24: change to “During these events other iodine species were also detected, as described below…”

These have been corrected.

Page 9, Line 6: should be coastal, not costal

These have been corrected.

Page 9, Line 17: “with ions of sulfuric acid” are the iodine compounds the ions? Or is the sulfuric acid? Also in line 18, I2O2.CH3SO3, which one is holding the charge?

It is not possible to know precisely which molecule holds the charge. In cases when there are neutral species like I_2O_3 or I_2O_5, the charge should be carried by HSO_4^- or $CH_3SO_3^-$. However, in cases like the $HNO_3 \cdot HSO_4^-$ we assume that the most acidic molecule holds the charge, in that case bisulfate (Hunter and Lias, 1998). Although we did not find gas-phase acidity values for HIO_3 in the literature, we do not consider this issue to be relevant in the context of this paper since the *m/z* would be exactly the same in cases like $H_2OS_4 \cdot IO_3^-$ or $HIO_3HSO_4^-$.

Page 10, R.10: what is M?

M is a stabilizing molecule (an energy-absorbing species), usually N_2 or O_2. This has been added to the text.

Page 11, Line 16, typo in listing of figures.

This is corrected.

Page 12, Lines 11-14: The first sentence suggests they are clusters but the authors conclude they are not. Please explain more carefully why they are not clusters.

The re-analysis of the CLOUD data showed that both clusters of the type $(NH_3)_m(H_2SO_4)_nHSO_5^-$ as well as $(NH_3)_m(H_2SO_4)_nSO_5^-$ are possible. The binding of ammonia-sulfuric acid molecules occurs via strong hydrogen bonds and we believe it is unlikely that SO_5^- could be bound by an additional interaction of the type SO_3^-—O_2 with $(NH_3)_m(H_2SO_4)_n$. This sentence has been added to the text.

Page 13, Line 4: “The latter…” using the word latter means there are only two phrases but there are three. Maybe change to “the last process”

This is corrected.

Figure 1: The positive ions have higher signals than the negative ions (amine is roughly 4 times higher than sulfuric acid). The authors state that the amine concentrations must be quite low (page 14, line 22) as amines are not seen in ion clusters. The ion signals say otherwise. Can the authors comment on this? Discussing the efficiency of detection for the APi-ToF would be very useful here.

Indeed, we agree with the observation that the signal of the positive ions is higher which was also reported by Boulon et al. (2010) who detected higher concentrations of positive ions at the Jungfraujoch. This could be due to the electrostatic interferences that we had with the building (Page3, line 30).

We should mention that the total ion counts (TIC) are not constant in the APi-TOF even if this could be expected assuming the ion production rate to be constant at the JFJ. It is possible that a change in the size distribution of the ions would lead to the ions falling out of the APi-TOF detection range.

Figure 2, last line of caption: The comma (or is it a period?) after SO5 - looks strange.

The coma was as subscript, this has been corrected.

Figure 3: The colors for HSO4 - and CH3SO3 - look the same on a printed page. Also the units for signal are inconsistent with the other graphs (ions s-1 vs ions/s).

The plots have been corrected

Figure 6: the top part of several lines are cut off (e.g., CSI and IO3-)

The plots have been corrected

Figure 7: What does τ mean on the bottom left map graph in B and D? Also the units need superscripts. What is R?

In Figures 7 and 8 τ is the absolute footprint in units $s \cdot m^3/kg$ representing the amount of time that an air mass stays in contact with the surface divided by the local air density, while R represents the difference between the τ for the event and the mean τ over the whole simulation period (one year). In this way, R can be used to identify special features of the transport of an air mass for a NPF event, Page 8 lines 28-33.

The units have been corrected.

Figure 8: same comments as figure 7

Please see previous answer.

References

Boulon, J., Sellegri, K., Venzac, H., Picard, D., Weingartner, E., Wehrle, G., Collaud Coen, M., Bütikofer, R., Flückiger, E., Baltensperger, U. and Laj, P.: New particle formation and ultrafine charged aerosol climatology at a high altitude site in the Alps (Jungfraujoch, 3580 m a.s.l., Switzerland), Atmos. Chem. Phys., 10(19), 9333–9349, doi:10.5194/acp-10-9333-2010, 2010.

Heinritzi, M., Simon, M., Steiner, G., Wagner, A. C., Kürten, A., Hansel, A. and Curtius, J.: Characterization of the mass-dependent transmission efficiency of a CIMS, Atmos. Meas. Tech., 9(4), 1449–1460, doi:10.5194/amt-9-1449-2016, 2016.

Hunter, E. P. and Lias, S. G.: Evaluate gas phase basicities and proton affinity of molecules: an update, J. Phys. Chem. Ref. Data, 27(3), 413–656, 1998.