Chemical characterization of atmospheric ions at the High Altitude Research Station Jungfraujoch (Switzerland)

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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.

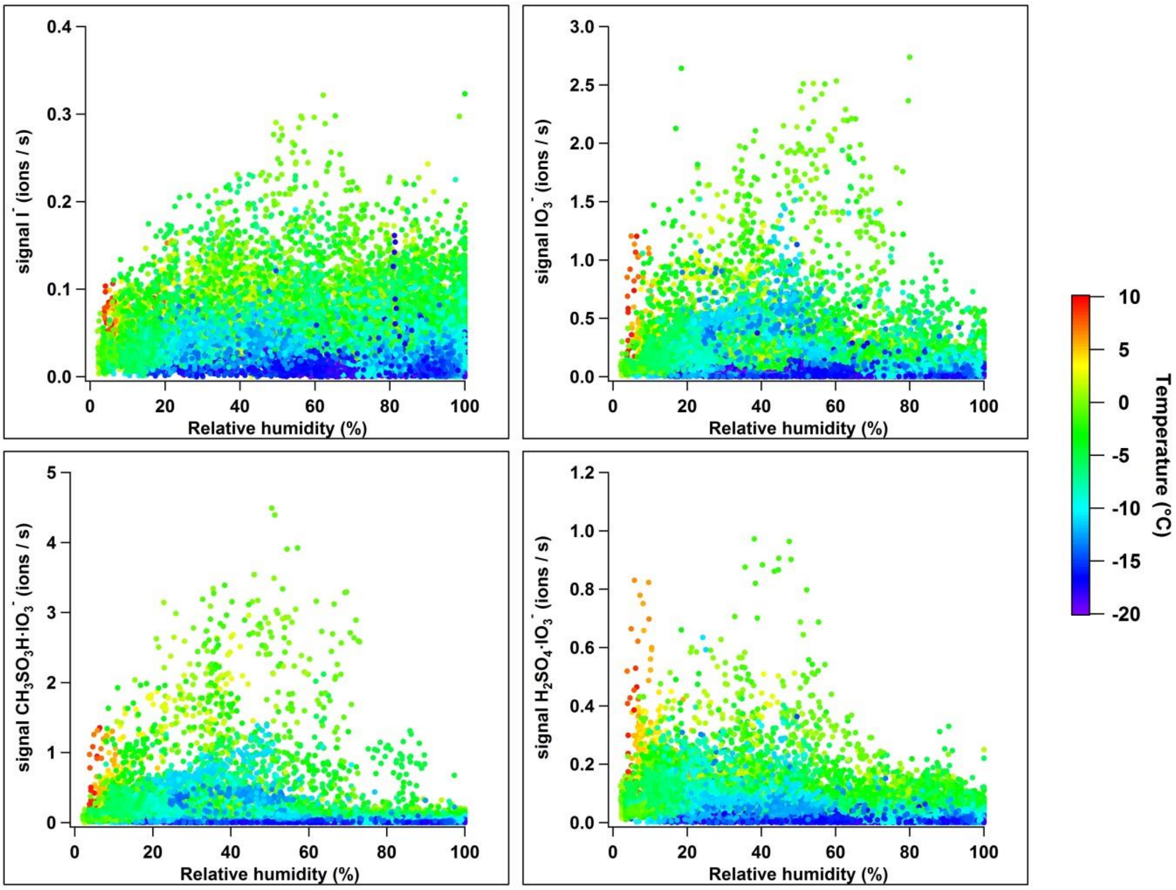

Figure R1. Signal of I^-, IO_3^-, $CH_3SO_3H \cdot IO_3^-$ and $H_2SO_4 \cdot IO_3^-$ against relative humidity and as a function of temperature. No clear dependence of the signal on relative humidity or temperature is observed as it was the case with sulfuric.

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).

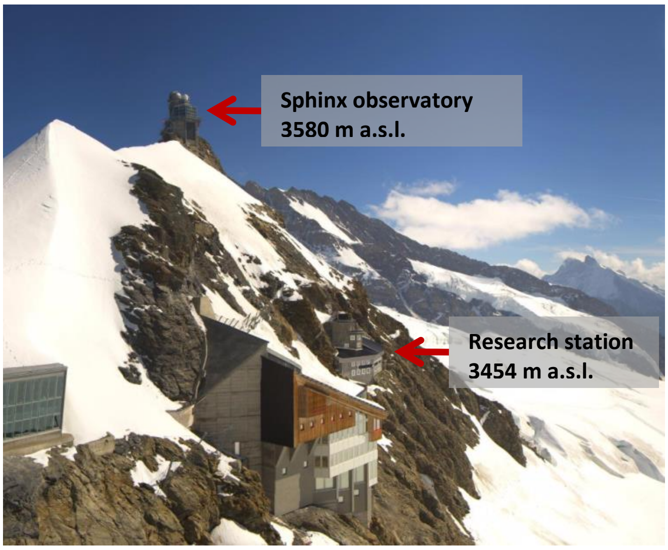

Figure R2 Picture showing the location of the Sphinx observatory and the Research station at the Jungfraujoch

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·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.

Comments Referee #2

This manuscript reports field observations of atmospheric ions measured with the Atmospheric Pressure interface Time-of-Flight (APiTOF) mass spectrometer at Jungfraujoch, Switzerland. Measurements were taken over nine months at high altitude. The authors discuss several classes of ions measured by APiTOF during the study, including bisulfate and halogen containing ions. The authors often observed a diurnal cycle for bisulfate containing ions, although they also occasionally observed their presence at nighttime. Halogen ion intensities were observed to be more abundant in the morning and evening, and the authors postulate photochemical degradation pathways as a reason for the low intensities during the daytime. The authors also provide some evidence for a marine or coastal origin of these ions through backward dispersion models.

This work is relevant because very few reports of ion composition at high altitude exist. The manuscript is within the scope of Atmospheric Chemistry and Physics and is written clearly with interpretable figures. This manuscript may eventually be publishable in Atmospheric Chemistry and Physics if the authors carefully address the comments below.

Major Comment:

In the discussion of halogenated species (section 3.2, page 8, lines 12-32) the authors postulate explanations for the observations of ions such as Br-, IO3 -, and CH3SO3 - at enhanced abundances at sunrise and sunset and during the nighttime (page 8, lines 12-14). The authors suggest that photochemical halogen chemistry may deplete the abundance of these ions during the daytime. Although it is possible this is the case, there appears to be an important assumption underlying the interpretation of the time dependent ion abundances that the authors have not addressed. Sulfuric acid is photochemically created during the daytime and its ion abundance increases substantially during the day. However, sulfuric acid also very effectively competes for the limited charge present in the atmosphere. As a result, and as illustrated in Fig. 2, most non-sulfur-containing ions are anticorrelated with bisulfate/sulfuric acid clusters. This anticorrelation does not necessarily indicate that the total concentration of these species (ion + neutral) is varying, only that the ion abundances are varying, potentially due to charge migrating to sulfuric acid clusters. The discussion of the halogens suggests that the observations of maximum abundances during solar minima are due to photochemistry removing the halogen-containing ions. However, it seems equally plausible that the enhanced abundances of halogen-containing ions are due to an overall decrease in sulfuric acid abundance that results in charge migrating to ions that otherwise could not outcompete sulfuric acid. The authors do very briefly allude to this subject in the discussion of Fig. 2 (page 6, line 25), but the discussion is insufficient. It seems to this reviewer that except for perhaps sulfuric acid it would be extremely difficult to draw any conclusions about chemical processes occurring from the time dependent measurements alone, as ion abundances do not necessarily indicate formation or destruction of chemical species.

This is an important issue. We agree that the charge redistribution can affect the intensity of the peaks in the spectrum and, as shown in the manuscript, sulfuric acid represented ~30% of the total signal during the day. We observed many incidences, when IO_3^- peaked with sunrise when sulfuric acid was still low. The trough throughout the day could indeed also be explained by charge transfer to sulfuric acid. Usually, at sunset another peak is observed. This case would also indicate a photochemical production of iodic acid whereby its daytime trend is not reflected in the ion signal, as brought up by the reviewer.

We changed the text as follows: The depletion of the ions is then presumably the result of photolysis or the reaction of their parent compound with halogen atoms or OH· radicals. Nevertheless, the observed diurnal pattern is also due to charge redistribution between iodic and sulfuric acid, as the latter has a strong diurnal variation (see above) and effectively competes for the limited charge. However, without measurements of neutral species it is not possible to discriminate between these two possibilities.

Other Comments:

1. The explanation of the back trajectories in Fig. 7B and 7D was not clear to this reviewer (page 9, lines 9-11). Does a positive value in the relative footprint back trajectory [R(%)] indicate that the amount of time an air mass spent over a region (e.g. Atlantic Ocean) was higher than a yearly average? Would it not make more sense for the average to be for all the days where ion abundances were measured? More generally, what fraction of air masses during the campaign (both when halogens were measured and when they were not) were transported over the Atlantic Ocean? It is not clear what magnitude of R(%) is considered “significant”. This section should be revised to improve clarity.

Yes, a positive value in R(%) indicates that the air mass spent more time in a particular region in comparison with the average back trajectory over a year.

We have recalculated the relative footprint by dividing the halogen ion event footprints by the mean over all the days where a high ion signal was measured (TIC ≥ 20 cps). Figure R3 present the resulting plots for the two events described in the paper (Fig.7 B and D). As it can be seen, the differences are minor for these single events, meaning that the general tendency of the halogen ions having mainly a maritime origin remains.

However, we do not consider that an average plot based on the days where ion abundances were measured would be more representative since this approach decreases significantly the number of residence times in certain areas. Therefore, the resulting relative footprint would be misleading. Thus, we conclude that comparing the halogen events with the average JFJ footprint is more meaningful and the obtained average plot (currently in the Manuscript) shows clearly a special feature of marine influence during the high halogen signal events against a small sample size of the total ion signal case.

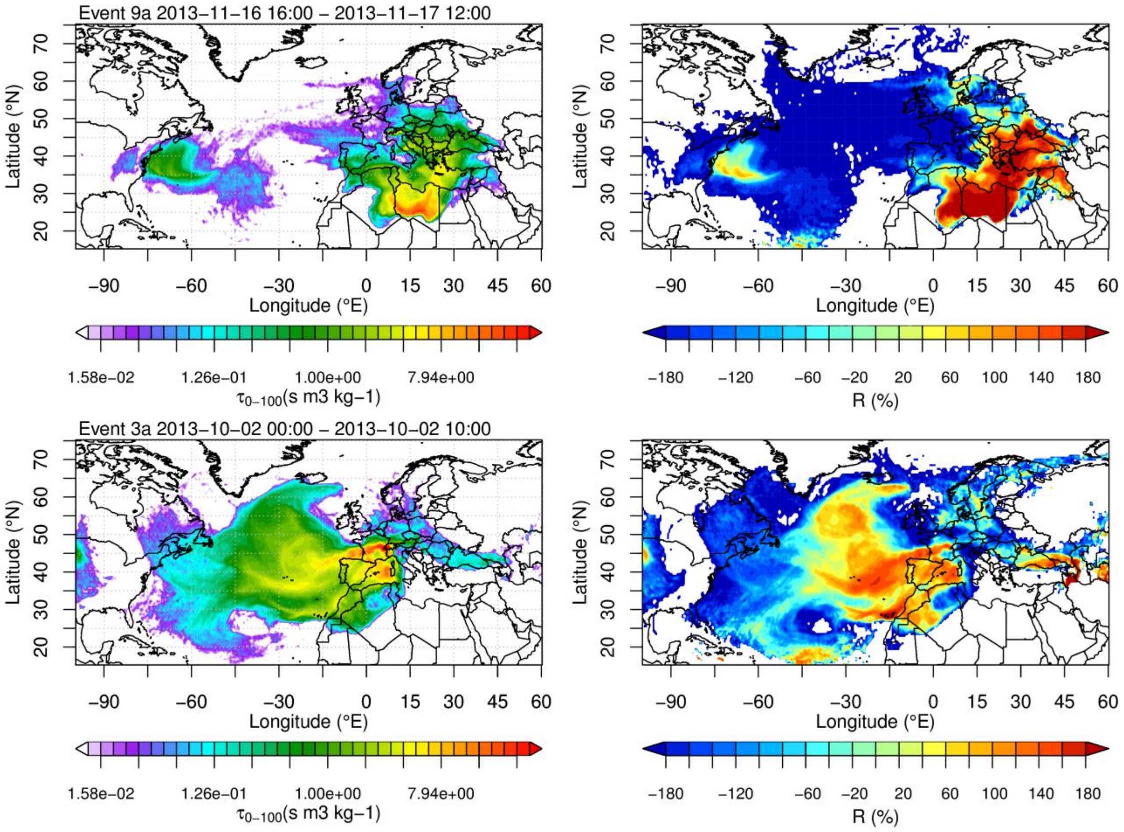

Figure R3. Recalculated relative footprint by dividing the halogen ion event footprints by the mean over all the days where a high ion signal was measured (TIC ≥ 20 cps).

2. How high is the authors' confidence in their assignment of elemental composition? For example, in Fig. 10A, the authors assign a number of peaks to ammonia-sulfuric acid clusters (page 14, lines 26-28). Elsewhere, the authors indicate that the positive ion spectrum contained less-oxygenated organics and did not observe any time-dependent compositional changes (page 6, lines 4-5). The authors should include additional discussion of the peak assignment protocol, including tolerances for agreement with theoretical monoisotopic mass, whether additional elemental composition assignments fall into the tolerance window for any given peak assignment (and why those assignments are discounted), and whether isotopic distributions were used to confirm some peak assignments. Finally, when listing assigned masses, the authors use varying significant digits: for example, on page 6, line 11, the authors discuss a peak at 163.123 Th and a peak at 192.1383 Th. Is the number of digits reported based on the confidence in the peak assignment? The rationale behind varying significant digits should be clarified in the manuscript.

We are highly confident about the assignment of the elemental composition due to the high resolving power of the APi-TOF, around 5000 Th/Th and the mass accuracy around 5 ppm for the full period of measurement and even around 2 ppm for the study of special cases (this information has been added to the text in section 2.2). All the *m/z* mentioned in the manuscript have a 4 digit precision, for clarity we add a zero to peaks like 163.123 (163.1230 Th). As example to show the accuracy of the measurements, we show in Figure R4 the fitting of $(H_2SO_4)_3HSO_4^-$ and

$(H_2SO_4)_3(NH_3)HSO_4^-$ and their corresponding isotopes. The notation below each molecular formula shows the mass and abundance of the main isotopes.

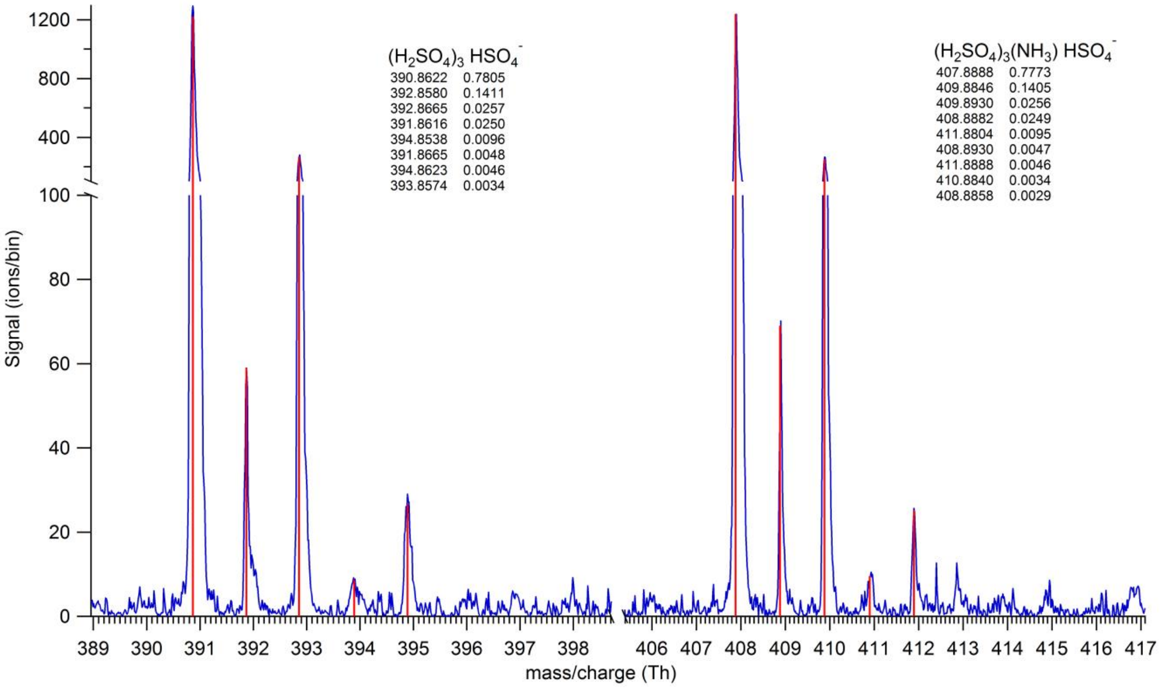

Figure R4. Fitting of (H2SO4)$_3$HSO$_4^-$ and $(H_2SO_4)_3(NH_3)HSO_4^-$ and their corresponding isotopes as example of the assignment of the elemental composition.

3. Because the authors are examining relative abundances of different ions, it would enhance the manuscript if authors included additional discussion of fluctuations in the total ion count (currently discussed briefly on page 5, lines 14-17). When changes in total ion current occur, do all peaks increase or decrease in abundance or are certain ions preferentially affected?

It is difficult to stablish causes for the total count (TIC) variation. We assume that most of the fluctuations were due to a change in the size distribution of the ions falling out of the APi-TOF detection range. In Figure R5 we compare the TIC with the cloud coverage (CSI) and the relative humidity (upper panels). As can be seen there is no clear dependence of the TIC on any of these factors. We also compared the TIC with representative ions like NO_3^- and HSO_4^-. In the last case there is some correlation which is expected considering the high signal of HSO_4^- in the spectrum. However in general terms it is still difficult to establish a clear dependence of the TIC on certain parameters.

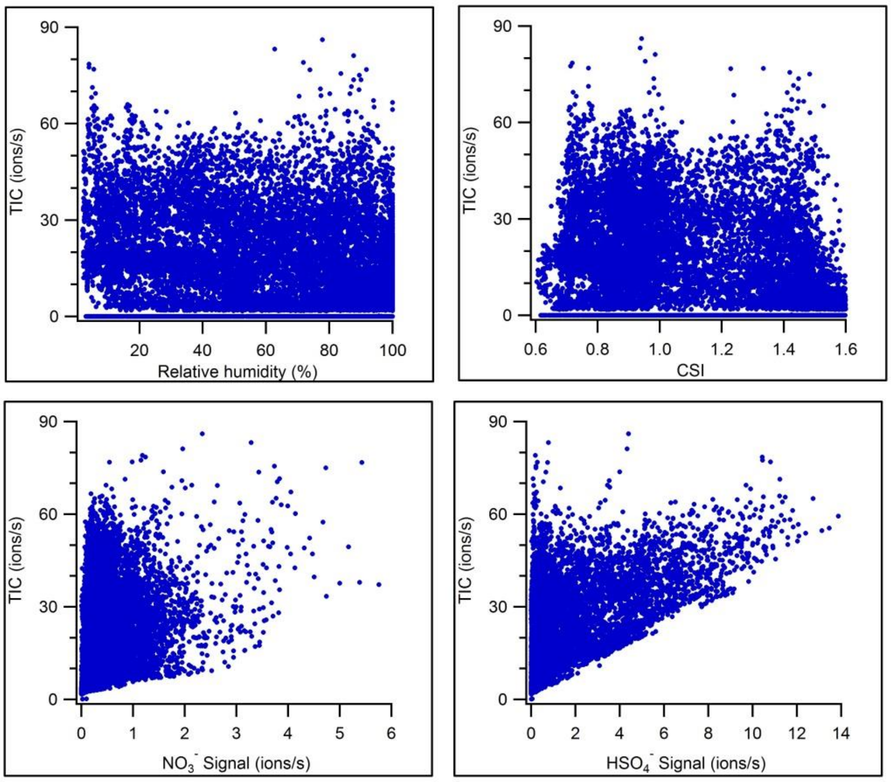

Figure R5. Scatter plots of the TIC against the cloud coverage (CSI) and the relative humidity (upper panels) and NO_3^- and HSO_4^- signals (lower panels).

4. In figures containing mass spectra, and especially in Fig. 10, the authors should more clearly indicate whether the mass spectrum showed is a positive mode or negative mode spectrum.

We added this information in the captions of Fig. 4 and Fig.10.

5. In the discussion of Fig. 10 (page 14, lines 24-25), the authors state that “the spectrum during nucleation time was deducted from the spectrum of the non-nucleation day.” Is this accurate, or was this stated backwards? If stated accurately, it suggests to this reviewer that the ions most abundant during nucleation should have negative abundances in the figure, which is not the case.

The difference is given as signal of nucleation days – non-nucleation days. We clarified this in the figure caption of Fig. 10. Thus, the positive signal represents the increase in signal (and therefore assumed concentration) of the clusters responsible of nucleation and absent during a non-nucleation event. In the case of Panel A the increase in signal is seen in the sulfuric acid-ammonia clusters. In the case of Panel B the increase is seen in a whole band of organic compounds.

Comments Referee #3

This paper reports field measurements of atmospheric ions over a nine month period in the free troposphere at Jungfraujoch, Switzerland. The study focused primarily on negative ions, i.e., producing seven categories of ions, relevant to two important topics (halogen chemistry and new particle formation, NPF) that the authors spent their efforts to elaborate. Atmospheric ions are of great interest to atmospheric chemistry, especially their composition, distribution, and roles in new particle formation and other ion chemistry. Issues and comments on this manuscript are listed below:

1. All the discussion in this paper is based on the results from negative ion measurements. The presentation of positive ions seems distractive rather than helpful to the overall conclusion of the study. It is suggested that only a few sentences would be enough to illustrate characteristics of positive ions.

We agree that the paper has an extended focus on negative ions. One of the reasons that lead us to measure only for a short period in this polarity was the higher variability observed in the negative mode compared to the positive mode (e.g. diurnal variation). The lower variability of the positive mode was also reported in previous ambient measurements (Ehn et al., 2010). Only one Panel of Figure 1 (Panel C) is dedicated to the positive ions accompanied by 10 lines of text. We think that it is worth to share the composition and features of the positive ions with the reader and that this is already quite short.

2. Figure 1 (a, b) is an average spectrum over the whole campaign period and detailed information on seasonal variation might be lost. The authors should provide at least some comparisons of the spectra among different seasons to demonstrate little variation among seasons so that this average method is validated.

We averaged only sunny days to ensure that we had measurements for the full time period of the averaging interval. This yielded in the average of 53 daytime spectra and 22 nighttime spectra. Separating these by season would give rather low statistics. In Figure R6 we show the spectrum of some of the averaged days corresponding to different months. As it is seen with the dotted lines, the main ions are the same and only a minor variation is observed in the small peaks.

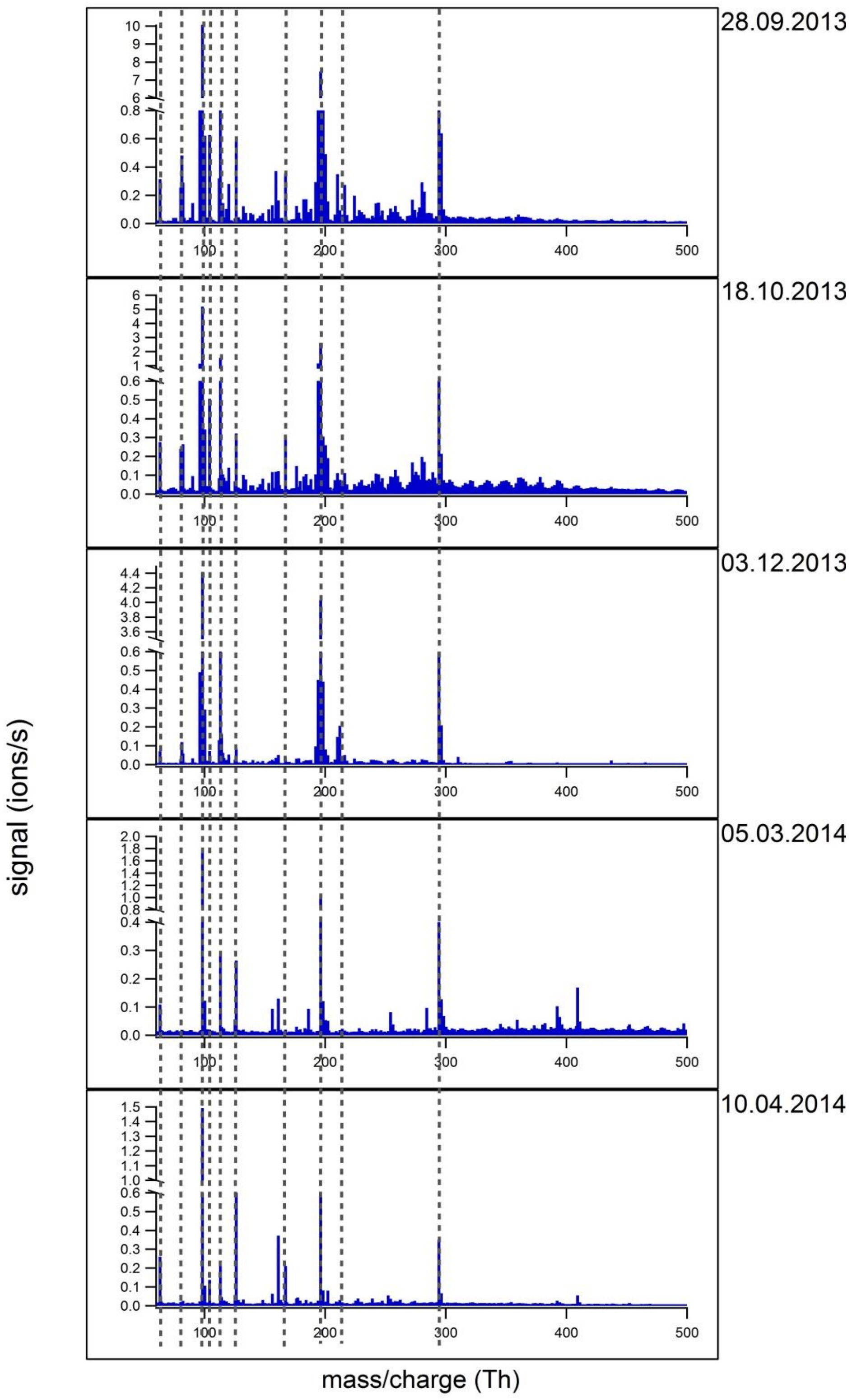

Figure R6. Spectrum of some of the averaged days corresponding to different months. No substantial seasonal variation is observed in the composition of the main ions.

We added this figure to the supplementary material and the following text: No substantial seasonal variation was observed in the composition of the main ions as shown in **Error! Reference source not found.**.

3. The authors proposed several plausible mechanisms for night time production of sulfuric acid. However, those mechanisms are for sulfuric acid molecules and the measurements are for ions only, not for molecules or clusters (no chemical ionization is applied). How this representation of molecule or cluster formation related to measured ions needs to be further illustrated.

HSO_4^- is most probably formed by an acid base reaction of sulfuric acid with an ion. The diurnal cycle of HSO_4^- is a clear indication that it follows the sulfuric acid concentration. In Fig.4 we presented a mass defect plot showing not only HSO_4^- but also its clusters, $(H_2SO_4)_{1-3}HSO_4^-$. This figure is one example of all the cases selected for the discussion of sulfuric acid measurement during night time. The presence of sulfuric acid clusters is another strong indication of the presence of neutral molecules.

In paragraph 3.3 we rephrased the text and it says now: Even though our measurements are restricted to ions, we believe that species such as sulfuric acid and MSA are formed as neutral channel species. The diurnal cycle of HSO_4^- presented in **Error! Reference source not found.** for example, is a clear indication that the ion follows the sulfuric acid concentration. Also, the presence of clusters of the type $(H_2SO_4)_{1-3}$ HSO_4^- or $(CH_3SO_3H)_{1-3}CH_3SO_3^-$ (shown in **Error! Reference source not found.**) is another strong indication of the presence of neutral molecules.

4. Figure 10b show higher signal intensities for m/z higher than 300, but it doesn't mean this higher portion is responsible for NPF, since there are still significant "residue" for m/z below 300 Th that may also possibly contribute to NPF.

The peaks detected at high masses, beyond 300 Th, are composed almost entirely of organic molecules. These molecules have been identified as highly oxygenated organics (HOMs) at the Jungfraujoch (Bianchi et al., 2016) and their very low volatility as well as their potential to drive new particle formation has been shown by others (Ehn et al., 2014; Kirkby et al., 2016; Riccobono et al., 2014; Zhang and Zhang, 2005). NPF occurs only when this high *m/z* portion increases remarkably. We cannot exclude that some of the lower masses ("residue") could also contribute to the NPF, especially since some of these peaks also correspond to highly oxygenated organic molecules (e.g. $C_5H_6O_6NO_3^-$). However, considering their saturation vapor pressure this is not very likely (see Tröstl et al., 2016). Most probably these are formed concurrently with the larger HOMs and later contribute to the growth of the freshly formed particles. This discussion has been added to the text.

5. Page 7, L21-22, Ehn et al. (2010) is not the first to report this ion of SO5-. In fact, Eisele et al., (JGR, 111, D04305, 2006) mentioned how this ion was produced in the atmosphere.

Experimental reports of SO_5^- are found even since 1988 (Huie et al., 1988) and we do not discard possible earlier experimental studies. However, to our knowledge Ehn et al. (2010) presented the first SO_5^- reports from ambient measurements. Eisele et al. (2006) speculated about SO_5^- formation as an explanation to the dip of NO_3^- and HSO_4^- in their measurements. The authors compared their ion measurements with model predictions and based on experimental studies about SO_5^- formation by Mohler et al. (1992), they suggested SO_5^- formation as possible explanation for a redistribution of charge in the sampled molecules under high SO_2 levels. However, the authors do not show or mention ambient measurements of SO_5^- .

6. Page 12, L1, please correct typos; L9, correct typos in “5 had an RH between 38- 62% and 16 a RH between 72-99%”; the last paragraph obviously present contradictive conclusions for the nature of SO5- and the authors need to provide some clarification

Can the reviewer specify which is the contradiction?

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Chemical characterization of atmospheric ions at the High Altitude Research Station Jungfraujoch (Switzerland)

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Abstract. The ion composition at high-altitude (345~~0~~4 m a.s.l.) was measured with an Atmospheric Pressure interface Time of Flight mass spectrometer (APi-TOF) during a period of nine months, from August 2013 to April 2014. The negative mass spectra were dominated by the ions of sulfuric, nitric, malonic and methanesulfonic acid (MSA) as well as SO_5^-. The most prominent positive ion peaks were from amines. The other cations were mainly organic compounds clustered with a nitrogen-containing ion, which could be either NH_4^+ or an aminium. Occasionally the positive spectra were characterized by groups of compounds each differing by a methylene group. In the negative spectrum, sulfuric acid was always observed during clear sky conditions following the diurnal cycle of sun irradiation. On many occasions we also saw a high signal of sulfuric acid during night time when clusters up to the tetramer were observed~~We also measured many events during night time where the signal of sulfuric acid was high and clusters up to the tetramer were observed~~. A plausible reason for these events could be evaporation from particles at low relative humidity. A remarkably strong correlation between the signals of SO_5^- and $CH_3SO_3^-$ was observed for the full measurement period. The presence of these two ions during both the day and the night suggests a non-photochemical channel of formation which is possibly linked to halogen chemistry. Halogenated species, especially Br^- and IO_3^-, were frequently observed in air masses that originated mainly from the Atlantic Ocean and occasionally from continental areas based on back trajectory analyses. We found I_2O_5 clustered with an ion, a species that was proposed from laboratory and modelling studies. All halogenated ions exhibited an unexpected diurnal behaviour with low values during day time. New particle formation (NPF) events were observed and characterized by 1) highly oxygenated molecules (HOMs) and low sulfuric acid or 2) ammonia-sulfuric acid clusters. We present characteristic spectra for each of these two event types based on 26 nucleation episodes. The mass spectrum of the ammonia-sulfuric acid nucleation event compares very well with laboratory measurements reported from the CLOUD chamber. A source receptor analysis indicates that new particle formation events at the Jungfraujoch take place within a restricted period of time of 24-48 hours after air

masses have had contact with boundary layer. This time frame appears to be crucial to reach an optimal oxidation state and concentration of organic molecules necessary to facilitate nucleation.

1 Introduction

Understanding the occurrence and composition of ions in the atmosphere is important because they regulate the electrical properties of the atmospheric medium, participate in ion-catalyzed and ion-molecule reactions and contribute to physico-chemical interactions, including ion-induced new particle formation (Schulte and Arnold, 1990). Ionization in the atmosphere takes place via different routes depending on the altitude. In the lower troposphere, ions are produced by radioactive emanation (mainly radon decay and gamma radiation), lightning and galactic cosmic rays (GCR), resulting in a production rate of about 2 ion-pairs cm^{-3} s^{-1} at sea level. This production rate increases with altitude, mainly due to increasing GCR intensity, reaching maximum rates of 35-50 ion-pairs cm^{-3} s^{-1} at 15 km (Arnold, 2008; Hirsikko et al., 2011; Smith and Spanel, 1996). The first observations of ions in the free troposphere and stratosphere were reported by Heitmann and Arnold (1983). By using ion mass spectrometers at high altitude (either on aircraft, balloons or rockets), they found that the main ions in the free troposphere were complex cluster ions containing H_2SO_4, H_2O, HNO_3, $(CH_3)_2CO$, and CH_3CN. In the last decade, the interest in atmospheric ions increased because of the potential impact of ion-aerosol-cloud interactions on climate (Hirsikko et al., 2011; Kirkby, 2007; Kirkby et al., 2011, 2016). Therefore, a number of laboratory and field studies have been conducted aimed at increasing our understanding of the precise role of ions in new particle formation. High altitude sites, which are often located in the free troposphere, represent an interesting region with a low condensational sink and low temperatures, i.e., conditions that facilitate the formation of new particles. In addition, the higher concentration of ions at high altitudes could enhance ion-induced new particle formation. Although several studies have reported on ions in the free troposphere and their link with new particle formation (Boulon et al., 2010; Rose et al., 2015; Venzac et al., 2008), they only presented the total ion concentrations but no chemical composition.

The low concentration of ions in the atmosphere has proven to be an obstacle in determining their chemical composition. Recent improvements in mass spectrometer detection limits now enables the measurement of the composition of ions and ion clusters at atmospheric concentrations and pressure using the Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer (APi-TOF) (Junninen et al., 2010). First atmospheric measurements with the APi-TOF were reported by Junninen et al. (2010) and Ehn et al. (2010), both for the boreal forest site Hyytiälä, in southern Finland. To our knowledge, no studies have yet been carried out to characterize the diurnal and seasonal trends and the chemical composition of air ions and ion clusters in the free troposphere. Here we present nine months of continuous measurements at the High Altitude Research Station Jungfraujoch (Switzerland), located at ~~3580~~ 3454 m a.s.l. The measurements were part of the NUcleation, CLoud and Aerosol Characterization Experiment (NUCLACE) campaign and complement studies on detailed new particle formation mechanisms (Bianchi et al., 2016) and longer-term new particle formation statistics (Tröstl et al., 2016). The aim of this work was to characterize the ion composition at this high altitude site and its possible link to source regions of the air masses and to new particle formation.

2 Methods

2.1 Site description

The High Altitude Research Station Jungfraujoch, Switzerland (JFJ, 3454 m a.s.l.; 46.55˚N, 7.98˚E; http:// hfsjg.ch) is often located in the free troposphere. The site is intermittently influenced by planetary boundary layer (PBL) air masses due to convective conditions and frontal systems varying from 80% of the time in summer to 60% in spring or autumn, and 40% in winter (Henne et al., 2009; Herrmann et al., 2015; Zellweger et al., 2003). The Jungfraujoch is also a well-known tourist destination which results in occasional contamination e.g. by cigarette smoke (Fröhlich et al., 2015). 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).

2.2 Instrumentation

The main instrument in this study was an Atmospheric Pressure interface Time-of-Flight mass spectrometer (APi-TOF, Aerodyne Research Inc. & Tofwerk AG). The instrument is described in detail by Junninen et al. (2010). The APi-TOF operates in two stages. The first stage consists of a pressure interface where either the positive or the negative ions are focused and guided by two quadrupoles and an ion lens through three pumped chambers. Here the sampled flow is reduced from atmospheric pressure to ~10^{-4} mbar. The second stage consists of a time-of-flight (TOF) mass spectrometer at a pressure of 10^{-6} mbar where ions are detected with a mass accuracy better than 5 ppm. The high sensitivity and resolution of the APi-TOF (resolving power around 5000 Th/Th) helps to detect and identify atmospheric ions in spite of their low concentrations. Air was aspired through a stainless-steel tube of 1 m length and 25.4 mm inner diameter at 10 L min^{-1} of which 0.8 L min^{-1} entered the instrument.

The APi-TOF was set for high sensitivity detection in the mass-to-charge (*m/z*) range between 60 and 1200 Th (short flight path in the TOF, V mode) and it was operated alternately between positive and negative mode, with ~80% of the measurements conducted in negative mode. For the mentioned m/z range it is assumed that the ions are within the detectable range of the APi-TOF and that the transmission is comparable for all the ions in this range. Data were analyzed using the software package *tofTools*, developed by the Department of Physics at the University of Helsinki. *TofTools* is implemented in MATLAB and allows the complete processing of the data, i.e., automatic averaging, mass calibration, baseline detection, peak deconvolution, and high resolution analysis. The noise level is around $0.5\text{x}10^{-3}$ cm^{-3} below 100 Th and decreases to 0.1×10^{-3} cm^{-3} at around 500 Th (Junninen et al., 2010). The assignment of the presented peaks was performed with an accuracy of 2 ppm for the analysis of special cases and considering isotopic distribution. An example of the peak fitting is provided in the supplementary material Figure S1.

Initially the APi-TOF was installed at the Sphinx observatory at the JFJ (3580 m a.s.l.) on the upper platform where all the monitoring instrumentation is located, but no negative ions were measured due to electrostatic interaction with the building structure, mainly the cupula. Therefore the APi-TOF was relocated at the JFJ research station (3454 m a.s.l.). Long-term observations at the Sphinx and the research station show no important variation in aerosol parameters (see Bukowiecki et al., 2016), therefore our measurements should be comparable with those of the instruments at the Sphinx.

The JFJ is equipped with a suite of permanently operated atmospheric monitoring instrumentation (see Bukowiecki et al., 2016). In addition, a nano scanning mobility particle sizer (nano-SMPS) was operated to determine the size distribution of freshly nucleated particles (Tröstl et al., 2016). Meteorological data (relative humidity, temperature, wind direction and global radiation) were obtained from the station operated at the JFJ by MeteoSwiss and were used at a time resolution of 10 minutes.

2.3 Transport simulation

To study the origin of different air masses sampled at the JFJ, backward dispersion calculations were carried out with the Lagrangian Particle Dispersion Model FLEXPART (LPDM, Version 9.02, Stohl et al., 2005). FLEXPART calculates the trajectories of an ensemble of air parcels (called particles) through the atmosphere. The model considers transport by mean flow, turbulence and sub-grid convection. By simulating thousands of air parcels an LPDM can be used in a quantitative way to derive source receptor relationships (SRR), establishing the effect of an emission release from a source on the atmospheric concentration at a receptor. In a receptor oriented approach, source sensitivities are derived from backward simulations, releasing air parcels at the location of the observation/receptor and following them backward in time. The derived SRRs provide information about when and where an air mass sampled at the receptor was in contact with the Earth's surface and potentially took up surface emissions.

Carbon monoxide emissions were also used as a tracer for anthropogenic activities and therefore planetary boundary layer (PBL) influence. Anthropogenic CO emissions were taken from the EDGAR-v4.2 emission inventory (http://edgar.jrc.ec.europa.eu/index.php) for the reference year 2008 (the latest available from the inventory).

Simulations were driven by 3-hourly operational analysis/forecast fields of the Integrated Forecasting System (IFS) of the European Centre for Medium Range Forecasts (ECMWF). The horizontal resolution of these inputs was 0.2° by 0.2° degrees in the Alpine area and 1° by 1° elsewhere. For the JFJ simulations, 50 000 model particles were released every 3 hours and traced back in the atmosphere for 10 days. Model output in the form of near surface residence times (referred to as footprints or source sensitivities) were then used to analyze where sampled air masses had been exposed to surface fluxes (emissions).

2.4 Determination of cloud coverage

In order to distinguish between sunny and cloudy conditions, the cloud cover was estimated with the Clear-Sky Index (CSI) described by Marty and Philipona (2000). The CSI is defined as the ratio between the apparent emittance and the theoretical clear-sky apparent emittance and is calculated from the atmospheric long-wave radiation, air temperature and relative humidity. As the combination of these three parameters is available continuously, the presence of clouds at or above the JFJ can be determined during day and night. A CSI ≤1 is considered as clear-sky (no clouds), while a CSI > 1 represents a cloudy sky (overcast). In addition, cloud coverage was also confirmed by comparing the CSI to pictures from cameras recording the panoramic view at the JFJ (panocam.skiline.cc/jungfraujoch and webcam.switch.ch/jungfraujoch/). These observations also help identify periods when the JFJ was *in cloud*.

3 Results and discussion

First we give an overview of the average composition of positive and negative ions at the JFJ. Thereafter, a few selected cases of special ion observations are presented. While this paper is strictly related to ions, for clarity we mention the ions with the name of the neutral molecule, e.g. sulfuric acid for HSO_4^-, nitric acid for NO_3^-.

For the full period of measurement we observed fluctuations in the total ion count (TIC). Fluctuations in the TIC were already noted by Boulon et al. (2010) who attributed this to the available ion precursors (e.g. radon) and the strength of the condensation sink. These fluctuations may also be due to the small mass range of ions measured with the APi-TOF, thus a change in the size distribution of the ions resulting in a different fraction of outside of the APi-TOF detection range could result in a TIC fluctuation. Still, this observation should not affect the qualitative analysis presented below.

3.1 Main ion composition

Negative ions were detected within an *m/z* range of 60 - 1200 Th. Representative mass spectra for clear sky conditions (CSI ≤1) are given in Figure 1. Panel A presents the average spectrum of 53 clear sky days during daytime (between 10:00 and 14:00 local standard time, LST) showing sulfuric acid and its clusters (dimer, trimer) as the main ions. Other important ions are SO_5^-, as well as the ions of nitric acid, methanesulfonic acid (MSA) and $C_3H_3O_4^-$ (most probably malonic acid). Panel B shows the average spectrum of 22 clear sky nights (between 22:00 and 02:00). In this case, sulfuric acid and its clusters were strongly reduced (although they are not completely absent), and the largest signal is from $CH_3SO_3^-$ followed by SO_5^-, nitric acid and malonic acid (including their clusters). During both the day and the night, we observed the presence of organics, identified as $C_{2-18}H_{1-22}O_{2-13}$, generally with high oxygen content. In the mass range 120-440 Th, organics occurred mainly in clusters with NO_3^- or HSO_4^-. Halogenated ions were found as well. Ions from iodine were mainly observed as IO_3^- and in clusters with either H_2SO_4 or MSA, while ions from bromine were detected only as Br^-.

These ions were present during day and night, although their signal was highest during sunrise and sunset. No significant seasonal variation was observed in the composition of the main ions as shown in shown in Figure S2.

Positive ions were identified in the *m/z* range of 70 - 300 Th. At low *m/z* most of the peaks were identified as protonated amines and oxygenated organics ($C_{3-14}H_{5-18}O_{1-6}H^+$). At high *m/z* (>120 Th) we found mostly N-containing ions that could not be unambiguously ~~undoubtedly~~ attributed to amines or oxygenated organics clustered with a nitrogen-containing ion (either an ammonium or an aminium). In general, the positive spectrum contained less oxygenated organics with no significant difference in composition between day and night. Schulte and Arnold (1990) reported that the main cation in the middle troposphere (3000 - 6000 m a.s.l.) was pyridine ($C_5H_6N^+$). We also measured this as one of the main cations together with aniline ($C_6H_8N^+$) and benzylamine ($C_7H_{10}N^+$). We do not present an average spectrum of the positive mode since we do not have sufficient data of clear sky days to generate an unbiased average spectrum. Occasionally, a sequence of peaks with an increasing number of methylene groups was observed as a clear pattern in the positive spectrum, mostly after a direct PBL contact (based on Herrmann et al., 2015); one example during 23 January 2013 is shown in panel C of Figure 1. Mostly during summer, some high intensity peaks, mainly at 163.1230 and 192.1383 Th, appeared with the first one being potentially identified as nicotine ($C_{10}H_{15}N_2^+$). The presence of these ions is most likely related to tourists smoking on the terrace of the JFJ station (Fröhlich et al., 2015).

Figure 2 shows the diurnal variations of the main negative ions normalized to the total negative ion count, averaged for 15 clear sky days (cloudless during the whole day). The figure classifies the ion counts into 7 groups: sulfuric acid (HSO_4^-, $H_2SO_4{\cdot}HSO_4^-$ and $(H_2SO_4)_2{\cdot}HSO_4^-$), nitric acid ($NO_3^-$ and $HNO_3{\cdot}NO_3^-$), MSA ($CH_3SO_3^-$, $CH_3SO_3H{\cdot}CH_3SO_3^-$, $CH_3SO_3H{\cdot}NO_3^-$ and $CH_3SO_3H{\cdot}HSO_4^-$), SO_5^- , malonic acid ($C_3H_3O_4^-$, $C_3H_4O_4{\cdot}HSO_4^-$ and $C_3H_4O_4{\cdot}\ NO_3^-$), others (identified ions, e.g. the halogen ions IO_3^-, Br^-) and non-identified ions. Approximately 40% of the total ion signal at the JFJ was identified for this time period. During the day time (between 08:00 and 18:00h) the percentage of identified ions increases to 60% with the sulfuric acid group representing around 35% of the total ion signal. However, during the night time when the rate of sulfuric acid formation is very low, the charge is redistributed and the "non-identified" category becomes the most relevant. This group includes mainly the highly oxygenated organics between 450-1200 Th. Such compounds were also observed in the boreal forest by Ehn et al. (2010) where the signals of organic ions tended to be stronger during the night time (again due to less competition by the sulfuric acid clusters).

Beside malonic acid, other organic species of low molecular mass were frequently measured, like $C_3H_5O_3^-$, $C_3H_3O_3^-$ (pyruvic acid), $C_2HO_4^-$ (oxalic acid), $C_4H_3O_4^-$ and $C_4H_5O_4^-$. Still, malonic acid was the main organic ion not only during the day but also during the night and during clear sky and cloudy conditions. Actually, under cloudy conditions some peaks were less affected, including organics (e.g. malonic acid) and nitric acid. For the latter, we even measured its water clusters (e.g. $H_2ONO_3^-$, $(H_2O)_2NO_3^-$). In fact, when we sampled inside clouds (based on CSI and cameras) and during day time, most of the ions were composed of organics clustered with NO_3^-. Also, all sulfur containing peaks were absent.

No significant difference was observed for the spectra in different seasons (winter and summer) except for a more frequent increase in the signals above 450 Th attributed to organics during summer time. Considering that the JFJ is more frequently under boundary layer influence during summer (Herrmann et al., 2015), it is expected that vertical transport of air masses may carry more organics during this season.

We frequently detected the presence of sulfuric acid during night time although its rate of formation is expected to be low. Figure 1 B and Figure 2 show that the signal of sulfuric acid does not disappear during the night. In addition, we observed ~35 night time events when the signal increased significantly with also clusters of sulfuric acid up to the tetramer being present (however, never beyond the tetramer). Figure 3 presents an exemplary time series of some main ions at the JFJ. From 6 to 11 and from 15 to 18 November a typical diurnal variation of HSO_4^- is observed which is affected by the cloud coverage (CSI < 1 meaning clear sky) and the global radiation. The period from 11 to 14 November shows cases when sulfuric acid was also measured during the night time. The signal of HSO_4^- increases due to photochemical formation around noon on 11 November after a change of wind direction and subsequent clearing up. High signals are then observed in the nights to 12 November as well as to 13 November. Although the time trend in the plot represents only HSO_4^-, in this particular event the clusters of sulfuric acid up to the tetramer were observed. Figure 4 shows this observation in more detail with a mass defect plot and compares this event with the ion composition observed during a typical night at the JFJ.The mass defect represents the difference between the exact and the nominal mass of a compound (Th). The dots represent the main peaks, where the size of a dot is linearly proportional to the intensity of the signal and the colors represent the nature of the ions or clusters. While Panel A presents a typical night (averaged between 22:00 and 02:00), Panel B illustrates the event of unusually high sulfuric acid signal in the night from 11 to 12 November. During a typical night, the main ions are composed of $CH_3SO_3^-$ (brown dots) followed by SO_5^- (pink dots). Also sulfuric acid (red dots) can be seen and even the trimer is detected in a typical night time spectrum ($(H_2SO_4)_2HSO_4^-$, *m/z* 292.8949). By contrast, in Panel B, the main ion is sulfuric acid followed by SO_5^- and $CH_3SO_3^-$. In this event, also the tetramer of sulfuric acid is detected ($(H_2SO_4)_3HSO_4^-$, *m/z* 390.8622). Although Panel A in Figure 4 shows a typical night time spectrum, it is important to mention that the $CH_3SO_3^-$ signal was low in some cases where the main ions were malonic and nitric acid (NO_3^-, $C_3H_3O_4^-$, $HNO_3{\cdot}NO_3^-$, $C_3H_4O_3{\cdot}NO_3^-$).

The SO_5^- ion was found permanently among the main anions. The first atmospheric measurements of this ion were reported by Ehn et al., (2010). They observed a close correlation between the SO_5^- and HSO_4^- signals in the Finnish boreal forest ($R^2 > 0.8$), with an increase in signal correlated to global radiation. The same behavior was also observed at the JFJ (R^2=0.88), albeit only for day time measurements (global radiation > 550 W m^{-2}). However, at the JFJ the signal of SO_5^- was also present during clear sky nights, as shown in Figure 3.

In addition, we found a remarkably high correlation of SO_5^- with $CH_3SO_3^-$ for the full sampling period with a R^2 = 0.87 during night time (zero global radiation) and R^2 = 0.75 during day time (global radiation > 550 W m^{-2}). No special dependencies on boundary layer influence (based on Herrmann et al., (2015)) were found. The correlation is plotted in Figure 5 for day and night time. As shown in the same figure, a high correlation between SO_5^- and HSO_4^- is also seen during day time. Comparing Figure 5A and B it seems that the correlation of SO_5^- with $CH_3SO_3^-$ during day is offset to higher SO_5^- implying an additional mechanism forming SO_5^- during the day. This is further discussed in section 3.3.2 below.

3.2 Halogenated species

Naturally occurring halogenated species in the atmosphere are usually linked to measurements in the marine boundary layer (MBL), especially for chloride and bromide, which are contained in seawater. Compared to chloride and bromide, iodide is usually observed at lower signals. It is incorporated as a nutrient by biological processes. Inorganic iodine originates from the decomposition of natural iodocarbons such as CH_3I and CH_2I_2 and the inorganic precursors HOI and I_2 (Simpson et al., 2015). Several studies have reported the presence of iodine oxide at different locations in the MBL. Simpson et al. (2015) summarized these observations which include measurements at Tenerife, Tasmania, Cape Verde, West Pacific and East Pacific. To our knowledge, there are no reports of bromide or iodide and its oxides in the atmosphere of continental and high altitude locations similar to the Jungfraujoch (at 3580 m a.s.l. and around 250 km from the nearest costal region, in the Mediterranean).

The halogenated species CF_3^-, Br^-, IO_3^-, $HNO_3\cdot IO_3^-$, $CH_3HSO_3\cdot IO_3^-$ and $H_2SO_4\cdot IO_3^-$ were detected regularly at the JFJ. The maximum signal of these ions was generally observed during 07:00-09:00 and 17:00-21:00, but occasionally high signals were also detected during night time (22:00-04:00). Figure 6 shows this temporal variation with the main species, IO_3^- and Br^-, from 11 to 16 March 2014 (additional time series see also Figure 7, C). The figure also presents the signals of HSO_4^-, $CH_3SO_3^-$ and SO_5^- as well as global radiation, RH and the cloud coverage (CSI) to provide an overview over the ambient conditions. The clear peaks in signal, mainly of IO_3^-, during sunrise and sunset and the strong decrease during noon suggests the occurrence of efficient photochemical halogen chemistry. The process could be initiated by the so-called halogen reservoir species X_2, HOX, XNO_2 or HX, with X being the halogen atom.

$$X_2, HOX, XNO_2, HX \xrightarrow{OH, HO_2, h\nu} X\cdot + \text{products} \qquad \text{R.1}$$

The depletion of the ions is then presumably the result of photolysis or the reaction of their parent compound with halogen atoms or OH· radicals. Nevertheless, the observed diurnal pattern is also due to charge redistribution between iodic and sulfuric acid, as the latter has a strong diurnal variation (see above) and effectively competes for the limited charge. However, without measurements of neutral species is not possible to discriminate between these two possibilities.

An additional observation in Figure 6 is the trend of $CH_3SO_3^-$ which anti-correlates with sulfuric acid and rather follows the trend of IO_3^- and Br^-. From 12 to 15 March the solar radiation was strong and the RH low, producing a typical diurnal cycle of sulfuric acid. However, the $CH_3SO_3^-$ signal decreases during the peaks of sulfuric acid and only increases around 18:00 following the recovery of IO_3^- and Br^-. SO_5^- follows a similar trend as $CH_3SO_3^-$ but less pronounced. This has to do with additional pathways of SO_5^- as discussed below. The close relationship of the time trends of MSA with Br^- and IO_3^- could indicate a mechanistic connection between these species, for example a formation of MSA linked with halogen-based chemistry. However, it can also be simply caused by charge redistribution to sulfuric acid generating a similar diurnal trend.

The presence of these halogen species suggests that air masses of marine origin were transported towards the JFJ. Backward dispersion calculations were carried out with the FLEXPART model (see Section 2.3) for days when the signal of the main ion IO_3^- was equal or higher than the 95th percentile of all its values during this campaign (24 events in total). During these events ~~also~~ other iodine species were also detected, as described below. The transport simulations revealed that the air masses had an extended surface residence time over the Atlantic Ocean and occasionally also over the Arctic, Mediterranean Sea and continental regions. Figure 7 shows two events when the halogen signals increased, specifically for Br^- and IO_3^-. Panel A shows the temporal evolutions of the ion signal on 2 October 2013 while panel B shows the surface residence time back trajectories for the same period of time. Panel B is divided into two subplots, i.e., an absolute footprint, τ, in s·m^3/kg (left) and a relative footprint R (%) (right). The first refers to the amount of time that an air mass stays at the surface, whereas the second is calculated as the difference between the mean event footprint and the mean footprint over the whole simulation period (one year) divided by the mean of these two. The relative presentation usually assists the identification of special features of a certain transport situation without being dominated by the generally decreasing residence time with distance to the site. Areas with negative (positive) values of the relative footprint correspond to areas with weaker (stronger) surface sensitivity than the annual average. The event shown in Fig. 7 represents a case in which the air mass sampled at JFJ was dominated by above average surface contacts over the Atlantic Ocean. This event represents a frequently occurring transport of air masses from the Atlantic Ocean towards the JFJ. Similarly, panel C shows the time series of elevated halogen ion signals during an event on 16-17 November 2013 where the air masses arrived from continental areas with possible influence from the Eastern Mediterranean Sea. This type of transport was less frequent, with a total of 6 events out of the total 24. Although most of the backward simulations suggest a marine and coastal origin of the precursors of halogenated ions, we do not discard the possible contribution from continental regions as it is observed from panel D of Figure 7**Error! Reference source not found.**. A combined footprint of all the events with high halogen signal at the Jungfraujoch is presented in Figure 8. This combined inverse-time calculation confirms that air masses are transported mainly from the Atlantic Ocean and even from the US east coast.

The detection of ions and clusters of marine origin is potentially relevant due to their observed participation in new particle formation (O'Dowd et al., 2002). However, no new particle formation events were observed at the JFJ where halogen species were involved in cluster growth (see below), even though these ions were detected frequently. This would imply that halogens may be "spectators" at high altitude, i.e. ions that are present, but do not participate in new particle formation.

3.2.1 Iodine species

Besides IO_3^-, its clusters with H_2SO_4 and CH_3SO_3H and organics (e.g. $C_7H_{15}N\cdot IO_3^-$) were observed. Several other iodine species were also found at the JFJ. These included I^-, IO^-, IO_2^-, and clusters of ~~IO,~~ I_2O_3 and I_2O_5 with ions of sulfuric acid or –MSA (e.g. $I_2O_5 \cdot CH_3SO_3^-$). The observation of I_2O_5 in clusters with $CH_3SO_3^-$ ~~MSA~~ and sulfuric acid confirms the presence of I_2O_5 in the atmosphere which was proposed from laboratory and modelling studies (Saunders and Plane, 2005). However, to our knowledge no studies have reported the presence of I_2O_5 in the atmosphere up to now. Saunders and Plane (2005) speculated that I_2O_5 could be photo-chemically formed via an oxidation chain of iodine atoms with O_3 in the gas phase:

$$\mathrm{I} + \mathrm{O_3} \rightarrow \mathbf{IO} + \mathrm{O_2} \qquad \text{R.2}$$

$$\mathbf{IO} + \mathbf{IO} \rightarrow \mathrm{OIO} + \mathrm{I} \qquad \text{R.3}$$

$$\mathbf{IO} + \mathbf{IO} \rightarrow \mathrm{I_2O_2} \qquad \text{R.4}$$

$$\mathbf{IO} + \mathrm{OIO}\ (+\mathrm{M}) \rightarrow \mathbf{I_2O_3} \qquad \text{R.5}$$

$$\mathrm{OIO} + \mathrm{OIO}\ (+\mathrm{M}) \leftrightarrow \mathrm{I_2O_4} \qquad \text{R.6}$$

$$\mathrm{I_2O_2} + \mathrm{O_3} \rightarrow \mathbf{I_2O_3} + \mathrm{O_2} \qquad \text{R.7}$$

$$\mathbf{I_2O_3} + \mathrm{O_3} \rightarrow \mathrm{I_2O_4} + \mathrm{O_2} \qquad \text{R.8}$$

$$\mathrm{I_2O_4} + \mathrm{O_3} \rightarrow \mathbf{I_2O_5} + \mathrm{O_2} \qquad \text{R.9}$$

In this oxidation chain, the molecules detected at the JFJ as clusters with $CH_3SO_3^-$, NO_3^- or HSO_4^- are colored in blue. According to quantum chemical calculations by Kaltsoyannis and Plane (2008) I_2O_4 would have a lower stability in the atmosphere compared to the other iodine-containing species. This may be the reason why we did not observe this species. Saunders and Plane (2005) assumed that iodine atoms are formed by a photochemical process. However, for IO, I_2O_3 and I_2O_5 we observed a similar time trend as for IO_3^- with a strong decrease during day (see Figure 6). This is further indication of night time halogen chemistry. However, without the measurement of neutral species we do not have the quantitative concentration data to further elucidate this process.

3.3 Production of sulfur containing species

In this section we provide some hypotheses to explain the observed formation of sulfuric acid during the night time and the observed correlation between $CH_3SO_3^-$ and SO_5^-. Even though our measurements are restricted to ions, we believe that species such as sulfuric acid and MSA are formed as neutral channel species~~, since we observed their clusters~~. The diurnal cycle of HSO_4^- presented in Figure 2 for example, is a clear indication that the ion follows the sulfuric acid concentration. Also, the presence of clusters of the type $(H_2SO_4)_{1-3}\,HSO_4^-$ or $(CH_3SO_3H)_{1-3}CH_3SO_3^-$ (shown in Figure 4) is another strong indication of the presence of neutral molecules.

3.3.1 Sulfuric acid during night time

The most important gas phase pathway for the production of sulfuric acid occurs via the reaction of SO_2 with the OH radical (Stockwell and Calvert, 1983) and is the reason for the well-known diurnal cycle of sulfuric acid:

$$\mathrm{SO_2 + OH\cdot + M \rightarrow HOSO_2\cdot + M} \qquad \text{R.10}$$

$$\mathrm{HOSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3} \qquad \text{R.11a}$$

$$\mathrm{HOSO_2\cdot + O_2 \rightarrow HSO_5} \qquad \text{R.11b}$$

$$\mathrm{SO_3 + H_2O + M \rightarrow H_2SO_4 + M} \qquad \text{R.12}$$

where M is a stabilizing (energy-absorbing) molecule, usually N_2 or O_2. However, this reaction cannot explain sulfuric acid formation during night time observed in a total of 35 events at the JFJ with especially high signals (with clusters up to the tetramer). An alternative production of sulfuric acid during night time can take place through the Criegee intermediates (CIs); CIs have been observed in field measurements in a boreal forest (Mauldin III et al., 2012) and at coastal regions (Berresheim et al., 2014) and can be formed through the ozonolysis of double bonds containing compounds (alkenes):

$$\mathrm{O_3 + alkene \rightarrow Criegee\ intermediate\ (CI)} \qquad \text{R.13}$$

About half of the CIs in reaction R.13 decompose and produce OH. In this case the SO_2 oxidation chain can proceed as shown in reactions R.10, R.11a and R.12 producing sulfuric acid. The other half of the CI are stabilized producing stabilized Criegee radicals (sCI) which decompose over a much longer lifetime. These sCI are able to oxidize SO_2 and therefore produce sulfuric acid (Mauldin III et al., 2012). Alkenes can be transported to the free troposphere by injection of polluted air masses from the planetary boundary layer. Such an injection also decreases the CO/NO_y ratio which is used as a proxy for the age of an air mass since boundary layer contact (Zellweger et al., 2003). The night time sulfuric acid signal was not correlated with the CO/NO_y ratio, therefore it is possible that Criegee intermediates are not the main mechanism for night-time sulfuric acid formation at the JFJ. We do not discard, however, the possible transport of isoprene or terpenes from rural areas, not detected by the CO/NO_y ratio.

Besides CIs, we also explored the possibility of particle-gas partitioning from preexisting particles leading to an increase of sulfuric acid in the gas phase. Figure 9 (A and C) summarizes the signal of sulfuric acid during day and night time as function of relative humidity and temperature. During day under photolytic production its steady state concentration is strongly decreasing from low to high RH. At night time, higher signals are observed below 40% RH and temperatures above -5˚C. Regarding the events when a high signal of sulfuric acid was observed during night, 14 out the 35 events were characterized by a significant drop in RH to levels in the range of 3-27% with an increase in temperature (never exceeding 5˚C). One example of these events is given in Figures 3 and 4. For these events we considered the possibility of stratospheric intrusion as the reason for the drop in RH. During these events the ozone concentration did not change significantly (65-90 ppbv) except for 5 of the events when O_3 increased to levels between 103-130 ppbv. However, an O_3 concentration in the range of 70-90 ppbv was observed in the Alpine region by Stohl et al. (2000) during stratospheric intrusion events, therefore O_3 cannot be considered a strong marker of a stratospheric intrusion at the JFJ. The radon concentration (Institute of Environmental Geosciences, University of Basel, http://azug.minpet.unibas.ch) was also investigated in order to detect a stratospheric intrusion, but no significant variation of radon was observed.

From the remaining events with high sulfuric acid signal during night time, 5 had an RH between 38-62% and 16 a RH between 72-99%. These events were characterized by snow fall, consequently we believe that evaporation of sulfuric acid from snowflakes occurred in the inlet of the APi-TOF because of an increase in temperature between ambient conditions and the laboratory. Therefore, we conclude that all the events of high sulfuric acid during night time we measured resulted from the evaporation from the particle phase due to a decrease in relative humidity and/or increase in temperature either in the atmosphere (events with low RH) or in the instrument (events with high RH). Indeed, this process is well known. As an example, Mauldin III et al. (1999) observed an increase in the gas phase concentration of H_2SO_4 with decreasing RH during evening and nighttime flights over the Pacific. The measured H_2SO_4 concentrations were approximately a factor of 10 higher (~$1x10^6$ to $10-11x10^6$ cm^{-3}) when the aircraft flew in dryer layers of air (RH < 10% and temperature ~-3˚C). They confirmed these observations with models and laboratory measurements showing that H_2SO_4 evaporates from the particle phase at low RH. Recently, Tsagkogeorgas et al. (2016) found in the CLOUD chamber, with experiments at RH between 0.3 and 10% and temperatures between -5 and 20 ˚C, that a decrease in RH and/or an increase in temperature induces particle shrinkage by evaporation of sulfuric acid resulting in almost one order of magnitude higher concentrations of sulfuric acid in the gas phase with respect to the background.

3.3.2 Methanesulfonic acid (MSA) and peroxomonosulfate radical (SO_5^-)

The peroxomonosulfate radical (SO_5^-) was first measured in the laboratory as a product from the reaction of O_3^- or CO_3^- with SO_2 (Möhler et al. , 1992; Salcedo et al., 2004) according to:

$$\mathrm{CO_3^- \cdot nH_2O + SO_2 \rightarrow SO_3^- \cdot mH_2O + CO_2 + (n-m)H_2O} \qquad \text{R.14}$$

$$\mathrm{SO_3^- \cdot nH_2O + O_2 \rightarrow SO_5^- \cdot mH_2O + (n-m)H_2O} \qquad \text{R.15}$$

with $0 < n < 2$. R.14 could also take place with O_3^- instead of CO_3^-.

Bork et al. (2013) concluded from quantum chemical calculations that the distance and the strength of the O_2-SO_3^- bond resembles more a molecular cluster than a covalently-bound molecule. A reanalysis of the data from the CLOUD chamber presented by Schobesberger et al. (2015) reveals the presence not only of $(NH_3)_m(H_2SO_4)_nHSO_5^-$ clusters but also

$(NH_3)_m(H_2SO_4)_nSO_5^-$, suggesting that SO_5^- as well as HSO_5^- are most likely molecules rather than clusters. 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 $(NH_3)_m(H_2SO_4)_n$.

Reactions R.14 and R.15 could explain the observations of SO_5^- during the day and night at the JFJ. The correlation of SO_5^- with $CH_3SO_3^-$ shown in the previous section implies another strong source of SO_5^- with a common precursor for these two ions. It is important to note that although we measured ions, the presence of MSA clusters is a strong indication of neutral chemistry involved in the formation of MSA (Figures 1 and 4).

Traditionally, the oxidation of dimethyl sulfide (DMS) is considered the exclusive source of MSA (Seinfeld and Pandis, 2006). Since DMS is mainly produced by marine phytoplankton, MSA is also related to marine emissions. Since oxidation of DMS produces both MSA and SO_2, a correlation between MSA and SO_5^- could be envisaged based on the reactions R.14 and R.15. However, this would imply that the contribution of anthropogenic SO_2 sources is small, in contradiction with studies showing that the JFJ is influenced by regional sources and PBL air masses (Herrmann et al. 2015; Bukowiecki et al. 2016; and references therein). Although the production of MSA derived from DMS is a photochemical process we did not observe a clear diurnal pattern in the MSA signal similar to sulfuric acid. MSA is often anti-correlated to sulfuric acid as discussed above (Section 3.2 and Figure 6). Berresheim et al. (2002) did observe fluctuating behavior of MSA overlapping the diurnal photochemical formation at Mace Head (Ireland). They attributed this to a sensitive dependence of the gas/particle partitioning on RH or temperature. During day time we observed elevated MSA in the gas phase at low RH but during night time no clear dependence on RH or temperature (except for very low temperature) was observed (Figure 9, B and D). Due to the variation in partitioning of MSA, a high correlation with the independent formation of SO_5^- (reactions R.14, R.15) seems questionable. As seen from Figure 5C during sunny days sulfuric acid and SO_5^- are well correlated. This fraction of SO_5^- was presumably formed from deprotonation of the peroxyradical HSO_5. This radical may be formed from another pathway of reaction R.11, that is by addition of O_2 to HSO_3 (R.11b) rather than H-abstraction (Gleason et al., 1987). This pathway seems reasonable as also HSO_5^- is observed. H_2SO_5 can be formed from the reaction HSO_5 + HO_2. As seen in Figure 5A the SO_5^- produced by this mechanism shifts the MSA - SO_5^- correlation to higher SO_5^- values during the day. Thus, there are three possible formation pathways of SO_5^-, a) reactions R.14 and R.15 occurring all the time; b) deprotonation of HSO_5; c) unknown process correlated with the formation of $CH_3SO_3^-$. The last process seems to be not directly influenced by photolysis. The measurement of the neutral species could shed some more light on this. Previous studies claim that there might be a missing source of MSA (Bardouki et al., 2003; Mauldin et al., 2003). Mauldin III et al. (2003) and references therein speculate about the oxidation of DMS involving halogen chemistry or the production of MSA by oxidation of species other than DMS (e.g. DMSO) to explain MSA measurements during night time. Bardouki et al. (2003) suggest heterogeneous reactions of DMSO on aerosols as a source of particulate methylsulfonate. Our observations shown in Figure 6 could support the hypothesis of a mechanism involving halogen chemistry. Often MSA decreases concurrently with the halogen species Br^- and IO_3^- during day while all three species are observed during the night. It is also interesting to note that we often observed methyl bisulfate ($CH_4O_4S^-$, 110.9758 Th) at the JFJ, which to our knowledge has not been reported in the atmosphere. We may speculate that the formation of methyl bisulfate and MSA proceeds via a similar reaction.

3.4 New particle formation (NPF) events

During the whole period of measurement (~ 9 months) we identified more than 30 new particle formation events. From these events, some were not measured with the APi-TOF due to technical difficulties. In total, 26 events were registered from which we identified two types of new particle formation processes: one involving sulfuric acid-ammonia clusters (H_2SO_4-NH_3, 7 events) and one through highly oxygenated molecules (HOMs, 19 events). The first of these is well established, and has been observed regularly in the atmosphere (e.g. Zhao et al., 2011). Occasionally, the sulfuric acid-ammonia clusters were also observed during days with no new particle formation. In these cases, the clusters did not grow beyond ~2nm, obviously because not sufficient condensable material was present.

The second type of events, triggered by HOMs, was observed more frequently at the Jungfraujoch, where almost all the measured organic molecules were highly oxygenated, with an O:C ratio between 1 and 1.25 (see also Bianchi et al., 2016). Kirkby et al. (2016) showed in laboratory experiments that new particle formation of HOMs can also proceed without participation of sulfuric acid. Our data (Bianchi et al., 2016) confirm that this also happens in the ambient atmosphere, as the HOMs normally are mostly clustered with NO_3^- and only very rarely with HSO_4^-, suggesting that the major pathway of new particle formation was through the HOMs while sulfuric acid contributed only to a minor extent to this new particle formation.

Figure 10 presents the difference between the average spectra of each of these two types of new particle formation events and the average spectrum of 21 sunny days without new particle formation (Panel A for the 7 events with sulfuric acid-ammonia clusters and Panel B for the 19 events with HOMs). For this figure, the spectrum during nucleation time was deducted from the spectrum of the non-nucleation day. In the higher mass range of Panel A, ammonia-sulfuric acid peaks are clearly visible such as $(H_2SO_4)_3NH_3HSO_4^-$ (*m/z* 407.8888), $(H_2SO_4)_4(NH_3)HSO_4^-$ (*m/z* 505.8562), $(H_2SO_4)_4(NH_3)_2HSO_4^-$ (522.8827), $(H_2SO_4)_5(NH_3)_2HSO_4^-$ (*m/z* 620.8501), $(H_2SO_4)_5(NH_3)_3HSO_4^-$ (*m/z* 637.8767), $(H_2SO_4)_6(NH_3)_2HSO_4^-$ (*m/z* 718.8175), $(H_2SO_4)_6(NH_3)_3HSO_4^-$ (*m/z* 735.8440) and $(H_2SO_4)_6(NH_3)_4HSO_4^-$ (*m/z* 752.8706) . However, HOMs at high *m/z* are also present, suggesting that these contribute to new particle formation in these events as well. In Panel B, sulfuric-acid-ammonia clusters are clearly absent. In contrast, elevated signals of compounds/clusters above *m/z* ~300 are observed, indicating that cluster formation of highly oxygenated molecules is driving new particle formation. Although some other organics are also observed to increase at lower masses, we consider it unlikely that these molecules contribute to the formation of new particles due to their relatively high saturation vapor pressure (Tröstl et al., 2016). Most likely these molecules are formed concurrently with the HOMs and contribute to the growth of the freshly formed particles. Also, we cannot exclude participation of stabilizing ammonia in the cluster growth of the neutral clusters since this would not be detected in the anions.

The JFJ data are in excellent agreement with laboratory data reported from the CLOUD experiment where sulfuric acid-ammonia clusters were observed to grow by the progressive addition of H_2SO_4 and NH_3 (Almeida et al., 2013; Kirkby et al., 2011; Schobesberger et al., 2015). Figure 11 demonstrates with a mass defect plot how closely the measurements at the Jungfraujoch (panel A) and the CLOUD chamber (panel B) resemble each other. In both cases, pure sulfuric acid clusters are dominant and the strongest signal was detected for the trimer $(H_2SO_4)_2HSO_4^-$. Although clusters of the type $(H_2SO_4)_m(NH_3)_nSO_5^-$ were measured in the CLOUD chamber, we did not observe them at the JFJ. A possible explanation could be the difference in RH. Kurtén et al. (2009) reported that under atmospheric conditions the hydration of HSO_5 increases its lifetime significantly enhancing the probability to act as nucleation precursor. During the event shown in Figure 11 the average RH at the JFJ was only 3% (temperature of 1.1˚C) in comparison with 40% RH in the CLOUD chamber (temperature of 5˚C). In the JFJ mass defect plot clusters involving amines (yellow dots) and iodate (cyan dots) are also present, but the dominant clusters have the composition $(H_2SO_4)_m(NH_3)_n \cdot HSO_4^-$ as in the CLOUD spectrum. Concentrations of amines must be quite low as they are strong bases and are expected to bind strongly to acids in the preexisting aerosol. Indeed, aminium compounds were found in the Jungfraujoch aerosol (Henning et al., 2003).

The Lagrangian Particle Dispersion Model FLEXPART (see Section 2.3) was used in time-inverse mode to detect the origin of the air masses transported during all the NPF events in order to determine the source receptor relationship (SRR). In addition, CO emissions were used as a tracer for emissions from anthropogenic activities, contained in air vented from the PBL. The back trajectories of all NPF events were compared to those of non-event days. We found that all NPF events (i.e., both the H_2SO_4-NH_3 and HOMs types), were related to an increase in CO concentration and SRR 12 to 40 hours before the arrival of the air mass at the JFJ, suggesting a PBL contact of the air mass within that time period (see also Bianchi et al., 2016). For all back trajectories, only a small increase in CO was found within 6 hours before arrival at the JFJ, suggesting no significant influence from local emissions during this period. Thus, in a restricted time frame of 1-2 days after PBL contact, precursor gases are transported to the Jungfraujoch and may trigger NPF if oxidation of these gases leads to sufficiently high concentration of HOMs and/or sulfuric acid.

4 Conclusions

We conducted continuous measurements of atmospheric ions for nine months at the High-Altitude Research Station Jungfraujoch (JFJ, 3450 m a.s.l.). The positive spectrum was composed mainly of cations of amines, predominantly pyridine, aniline, and benzylamine, as well as of organic molecules which showed a regular pattern with increasing CH_2 moieties in the mass spectra. No strong diurnal behavior was observed, which is in agreement with observations by Ehn et al. (2010). The anion spectrum was usually dominated by sulfuric acid and its clusters, as well as nitric acid, SO_5^- and $CH_3SO_3^-$. The latter two were most abundant during night time. Likewise, small organic molecules were detected frequently but no clear dependence on meteorological conditions nor diurnal cycle was found to be associated with their occurrence. During the total sampling period malonic acid was the most important organic compound besides MSA. Sulfuric acid was frequently detected also during night time and in some cases the signal was so high that even the tetramer was detected. The most likely explanation is that the measured sulfuric acid resulted from evaporation from the particle phase in the atmosphere under low RH conditions or in the instrument during events with high RH and snow fall.

We found a remarkably high correlation between $CH_3SO_3^-$ and SO_5^- ($R^2 = 0.87$) for the full measurement period. This correlation was not sensitive to boundary layer influences, as we observed high correlations at free tropospheric and boundary layer influenced conditions. This correlation points to a common precursor for these two molecules. Considering DMS as common source would imply that all SO_2 in the JFJ is derived from DMS excluding anthropogenic sources in contradiction with several studies that show local and PBL influence at the JFJ. Moreover, the almost permanent occurrence of SO_5^- and $CH_3SO_3^-$ during night time contradicts the typical photochemical production of MSA. Therefore, we conclude that an additional channel for MSA and SO_5^- (probably HSO_5) formation should be considered.

We frequently measured halogenated species with occasional events of high signals when more species could be detected. Backward transport simulations linked these events mainly with the Atlantic Ocean as source region although also continental influence was observed. Besides IO_3^- we also measured I_2O_5, a species not reported so far in the atmosphere. Their signals as well as that of Br^- rapidly decay when the sun rises and stay low during sunny days, without any other halogenated ions appearing instead. The mechanism of their formation and diurnal variation of these ions is unclear. Parallel measurements of neutral halogenated species need to be performed to elucidate their precursors.

Two types of new particle formation events were identified at the JFJ, one through sulfuric acid - ammonia cluster formation and a more frequent one via highly oxygenated molecules which were normally clustered with nitrate and only occasionally with sulfuric acid. The sulfuric acid-ammonia cluster formation during these nucleation events at the JFJ compared very well with laboratory experiments at the CLOUD chamber at CERN, confirming the relevance of this mechanism for ambient nucleation. New particle formation of HOMs was evidenced by an enhancement of ions above *m/z*=300 Th. Such new particle formation that is primarily based on HOMs without significant participation of sulfuric acid was very recently found in the CLOUD experiment (Kirkby et al., 2016) and confirmed at the Jungfraujoch (Bianchi et al., 2016). New particle formation events take place at the Jungfraujoch 1-2 days after previous air mass contact with the PBL. This time frame appears to be needed to oxidize organic compounds transported towards the Jungfraujoch and trigger a HOMs based NPF.

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FIGURES

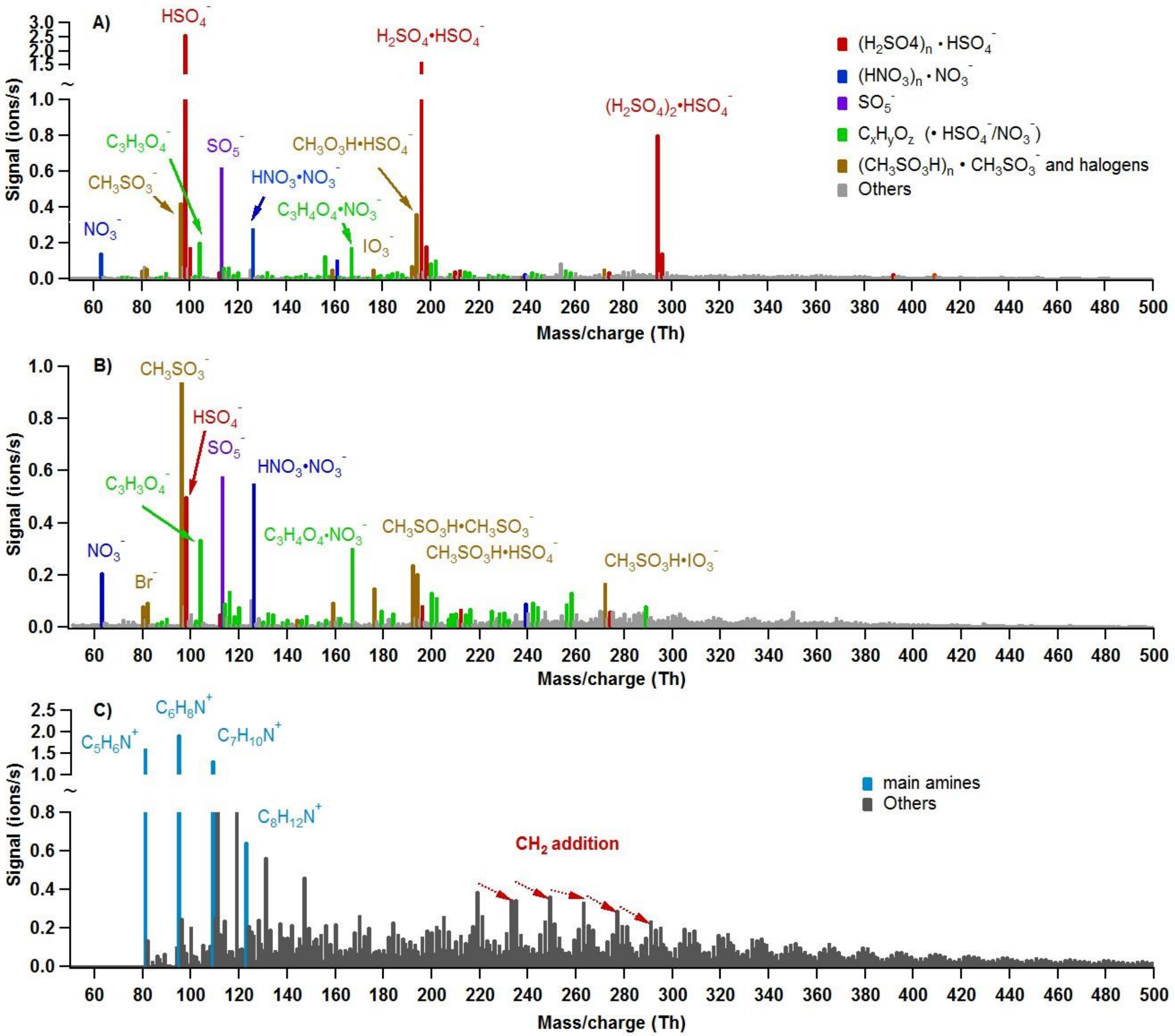

Figure 1. Representative mass spectra of ions from the Jungfraujoch. A) Average day time spectrum of negative ions from 53 cloudless days between 10:00 and 14:00. B) Average night time spectrum of negative ions from 22 cloudless nights between 22:00 and 02:00. C) Average spectrum of positive ions between 10:00 and 14:00 on 23 January 2013.

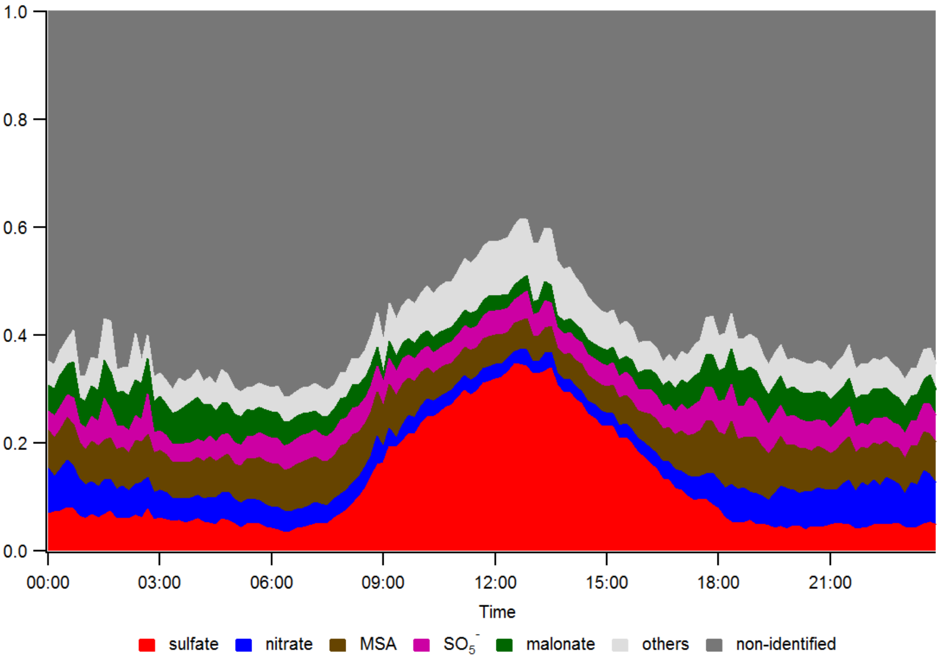

Figure 2. Average diurnal variations of the main negative ions at the JFJ over 15 days of clear sky normalized to the total negative ion count. Ions and clusters are grouped as follows: Sulfuric acid (HSO_4^-, $H_2SO_4{\cdot}HSO_4^-$ and $(H_2SO_4)_2{\cdot}HSO_4^-$), nitric acid ($NO_3^-$ and $HNO_3{\cdot}NO_3^-$), malonic acid ($C_3H_3O_4^-$, $C_3H_4O_4{\cdot}$ HSO_4^- and $C_3H_4O_4{\cdot}$ NO_3^-), MSA ($CH_3SO_3^-$, $CH_3SO_3H{\cdot}$ $CH_3SO_3^-$, $CH_3SO_3H{\cdot}NO_3^-$ and $CH_3SO_3H{\cdot}HSO_4^-$), SO_5^-, others (identified ions) and unknown (non-identified ions including ions in the *m/z* 450-1200 range).

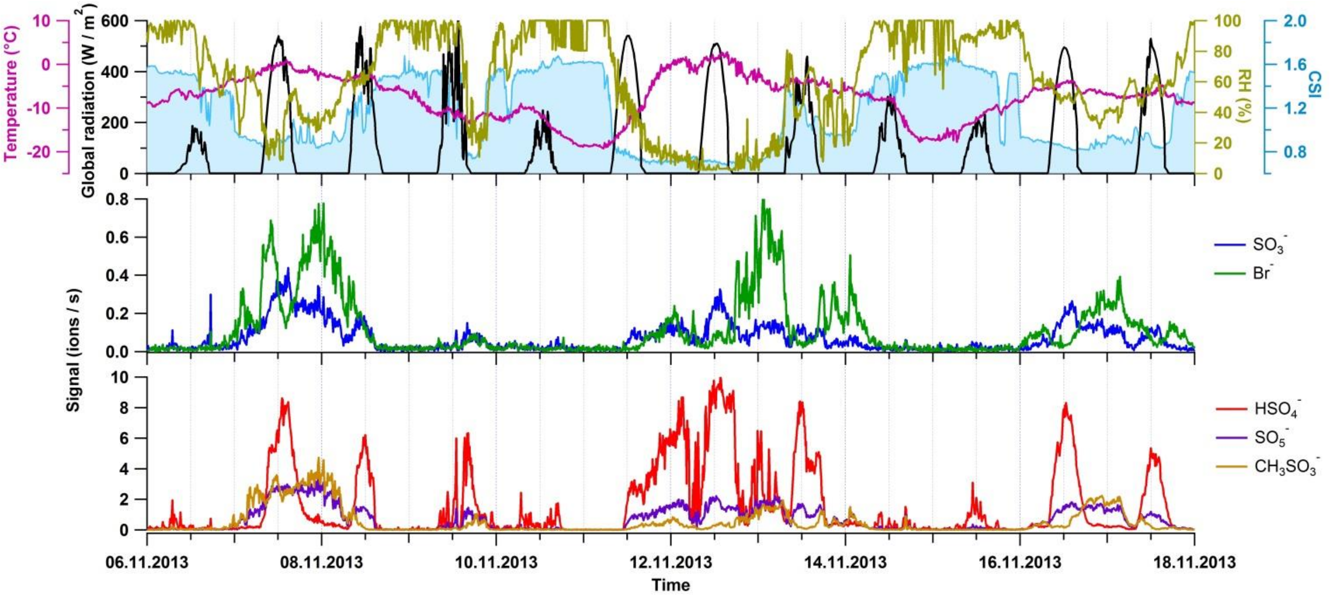

Figure 3. Time series of major ions and meteorological parameters from 6 November to 18 November. Upper panel: Global radiation (W/m^2), air temperature (°C), relative humidity (%) and clear sky index (CSI). Middle and lower panel: Br^-, SO_3^-, $CH_3SO_3^-$, HSO_4^- and SO_5^-.

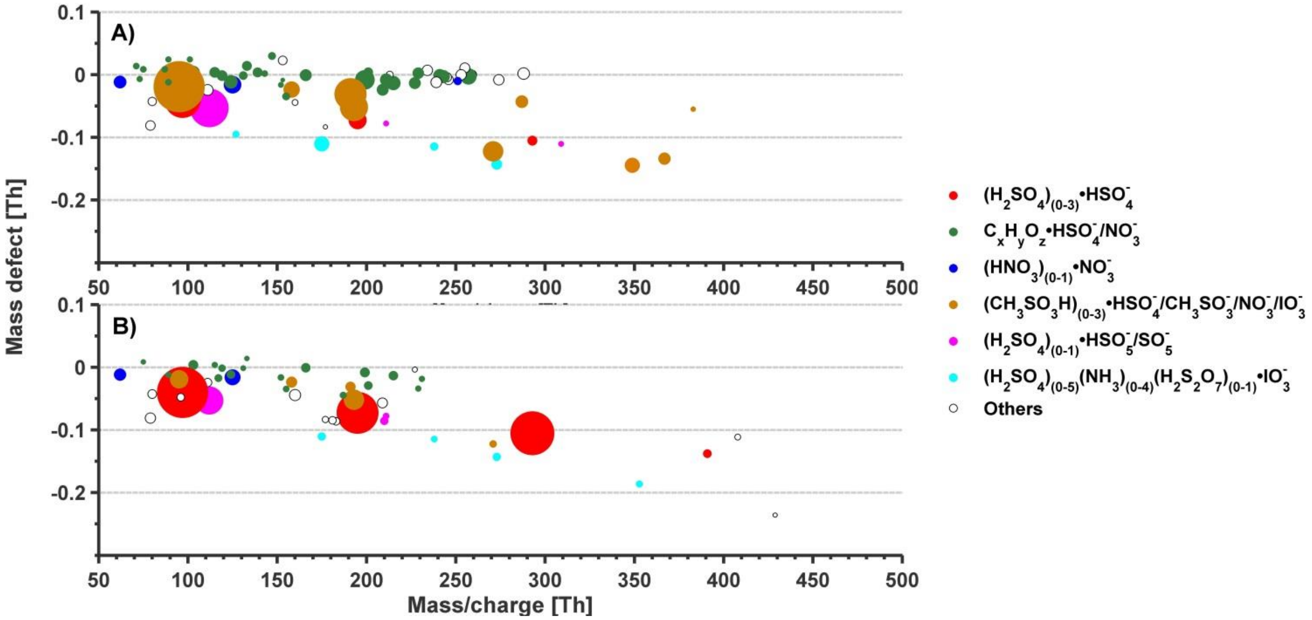

Figure 4. Comparison of two different night time spectra in negative mode between 22:00 and 02:00. A) Typical night spectrum, exemplified for the night from 9 to 10 March 2014. B) Spectrum with high sulfuric acid signal in the night from 11 to 12 November 2013.

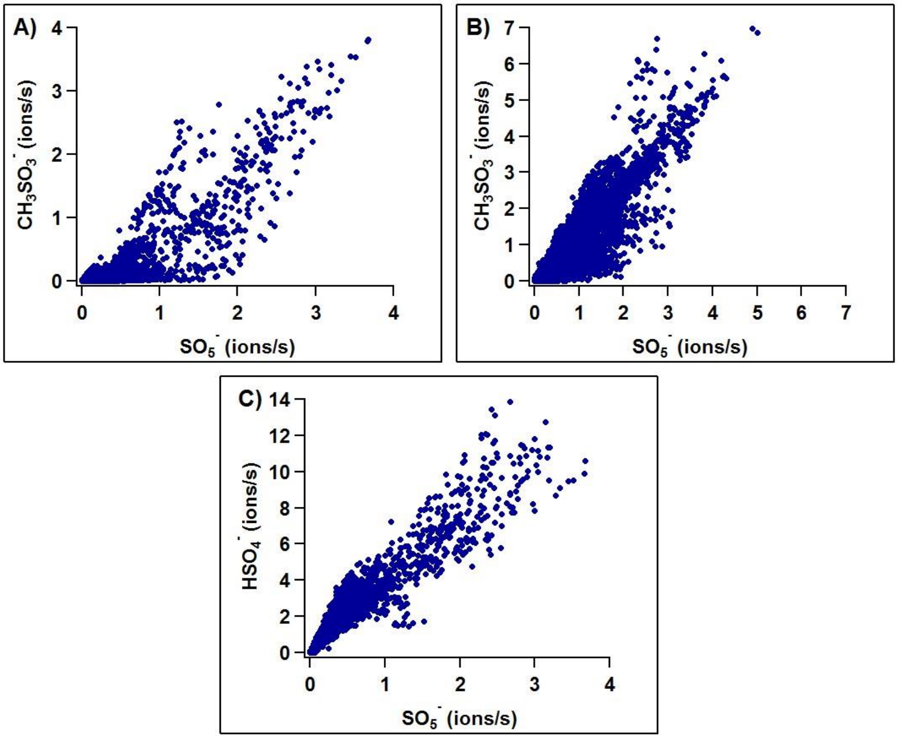

Figure 5. Correlations of SO_5^- with $CH_3SO_3^-$ and HSO_4^-
A): Scatter plot between SO_5^- and $CH_3SO_3^-$ ions during day time, $y = -0.14 + 0.78x$ and $R^2 = 0.75$.
B): Scatter plot between SO_5^- and $CH_3SO_3^-$ ions during night time, $y = 0.028 + 1.24x$ and $R^2 = 0.87$.
C: Scatter plot between SO_5^- and HSO_4^- ions during day time, $y = 0.468 + 3.49x$ and $R^2 = 0.88$.

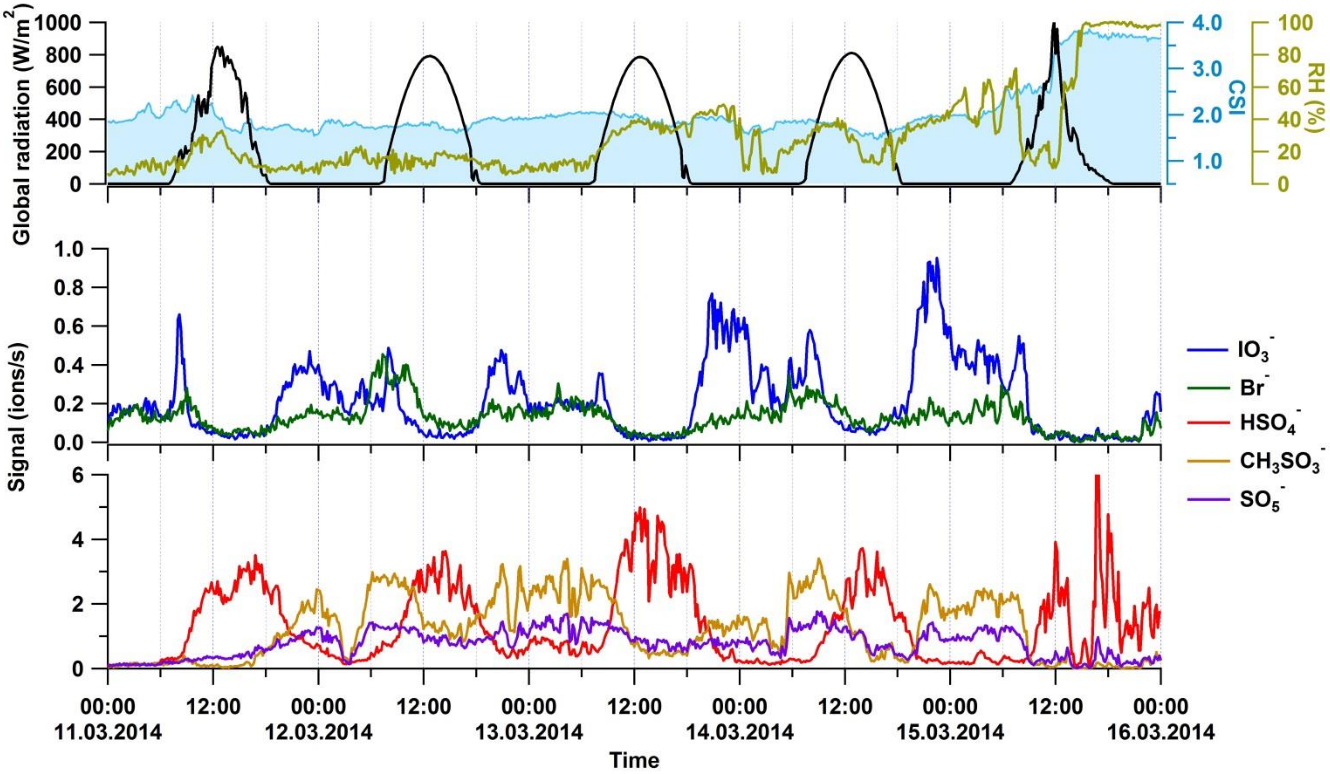

Figure 6. Time series from 11 to 16 March illustrating halogen chemistry. Global radiation, RH and cloud coverage are shown in the top panel. The decrease in signal of Br^- and IO_3^- during noon in the middle panel implies photochemical reactions on the precursors of these ions. The lowest panel shows the anti-correlation of sulfuric acid with $CH_3SO_3^-$ and SO_5^-.

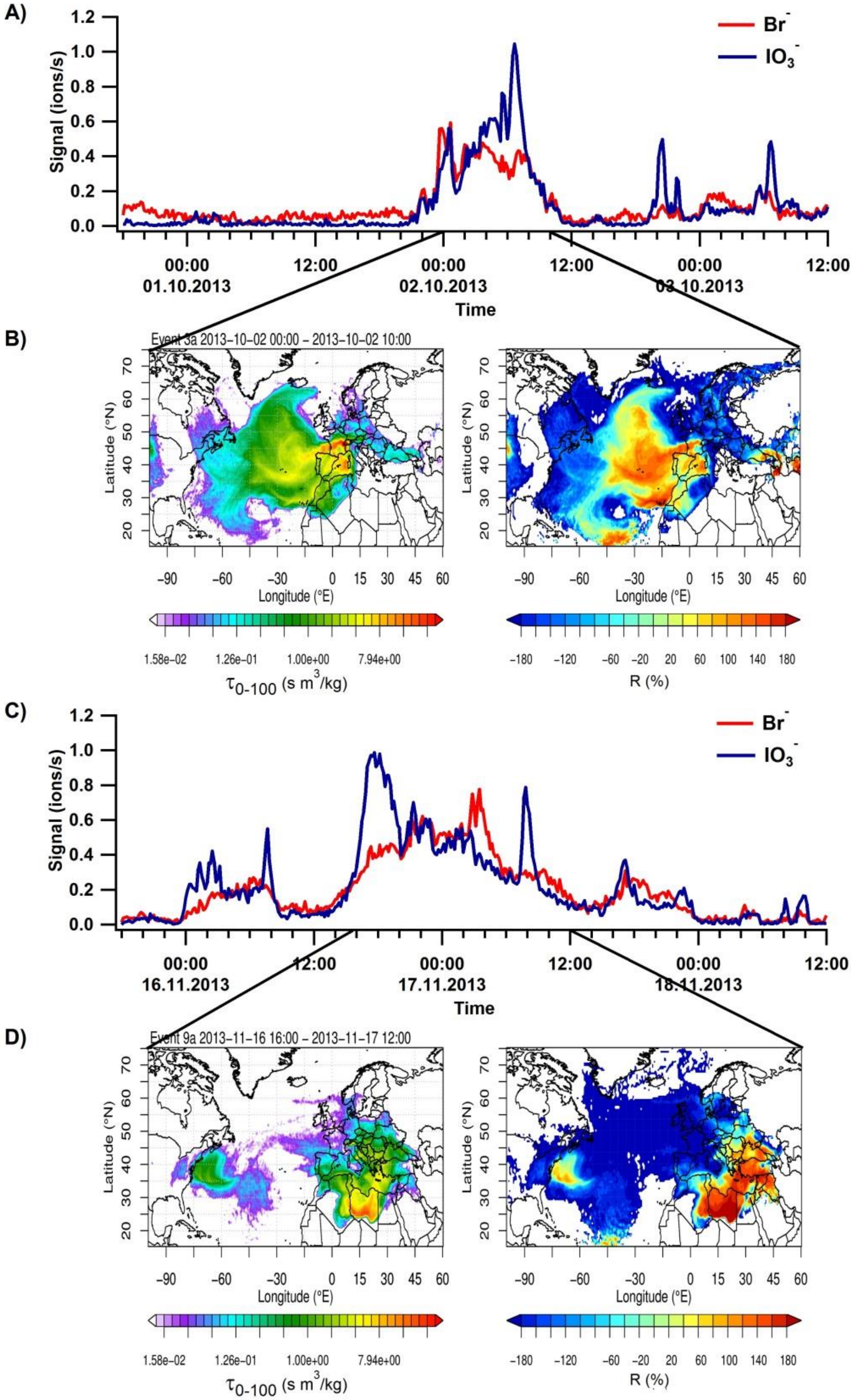

Figure 7 Examples of two events with high Br$^-$ and IO$_3^-$ signal and back trajectories for surface residence time. A) and B) Air masses from the Atlantic, C) and D) air masses from the Mediterranean. The black lines denote the time period for the trajectory analyses shown in Panel B and D.

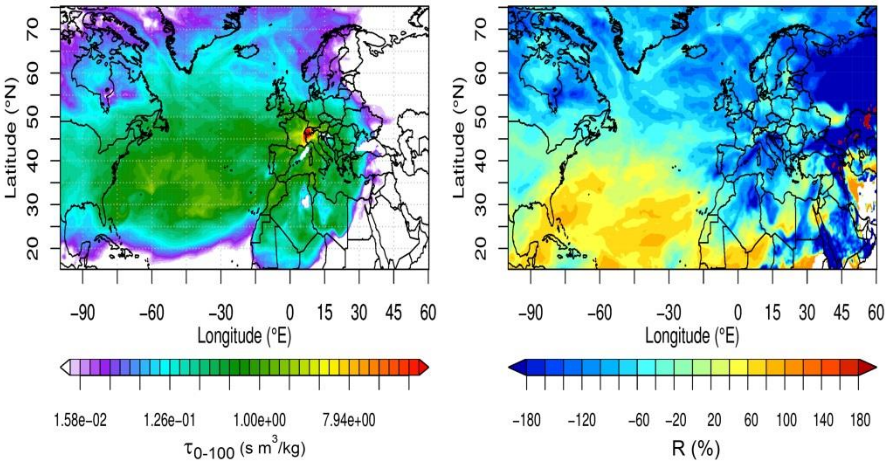

Figure 8. Combined footprint from all events with high halogen signal (IO_3^- and Br^-).

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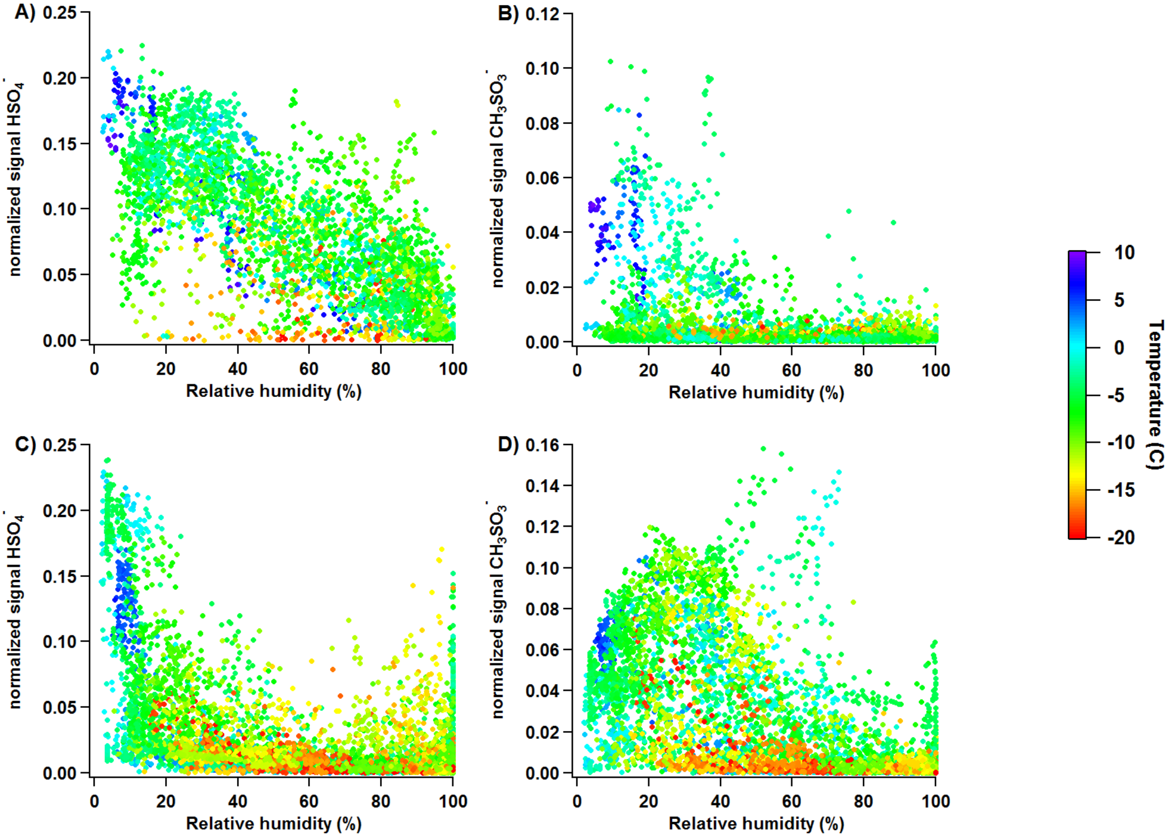

Figure 9. Dependence of HSO_4^- and $CH_3SO_3^-$ on relative humidity, as a function of temperature during the daytime (A and B) and nighttime (C and D). The signal was normalized to the total ion counts.

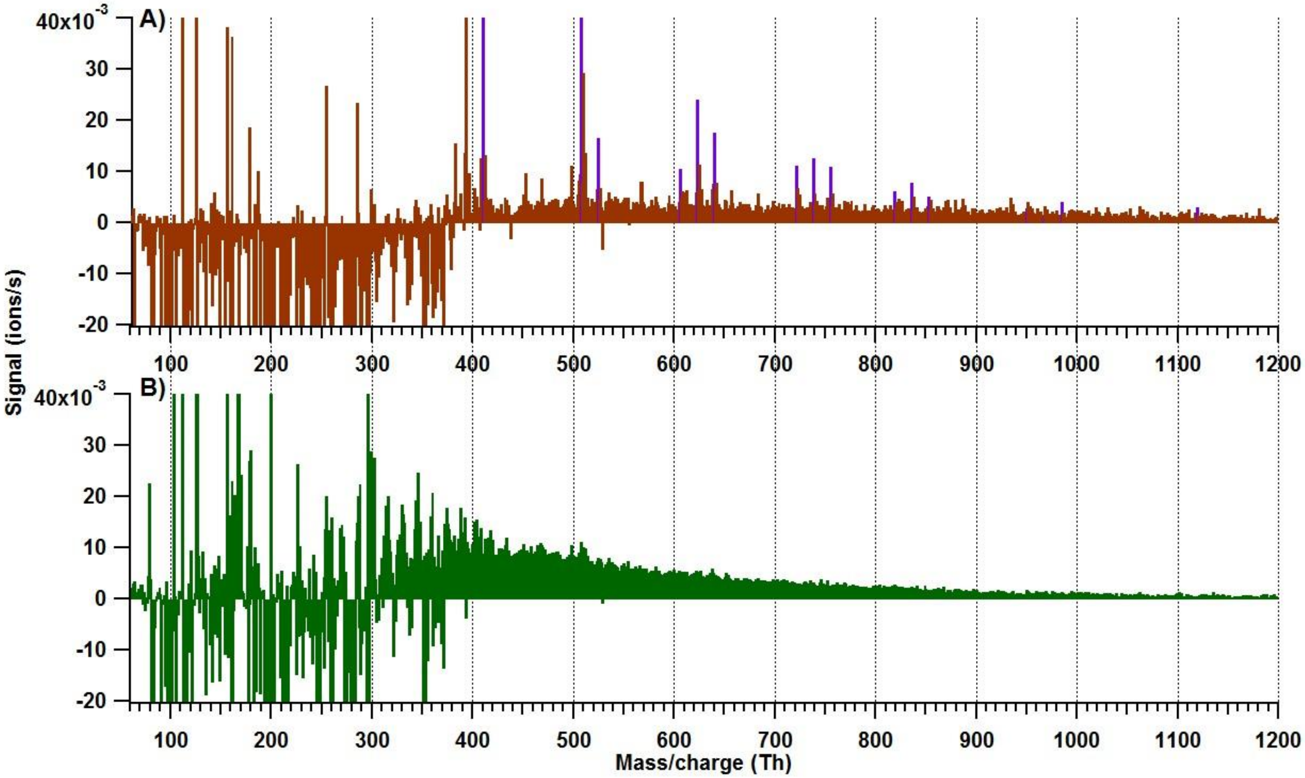

Figure 10. Difference of the negative mode mass spectra between two types of new particle formation and the average of 21 non-new particle formation sunny days (average signal of nucleation days – non-nucleation days). Panel A: 7 new particle formation events with H_2SO_4-NH_3 clusters (purple peaks); Panel B: 19 new particle formation events with HOMs).

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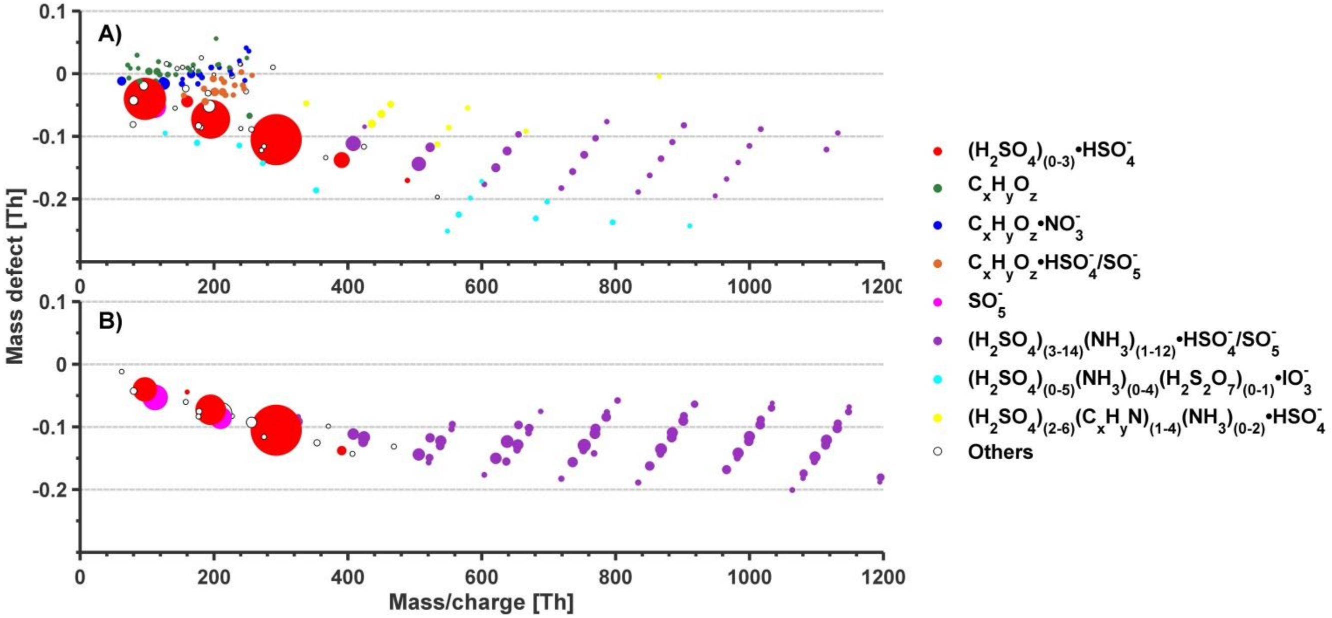

Figure 11. Comparison of ambient and laboratory measurements. a) Mass defect plot from the Jungfraujoch on 12 November 2013 from 08:30 to 12:30. B) Mass defect plot from a laboratory experiment at the CLOUD chamber involving H_2SO_4 and NH_3 clusters (adapted from Schobesberger et al., 2013).

SUMPPLEMENTARY INFORMATION

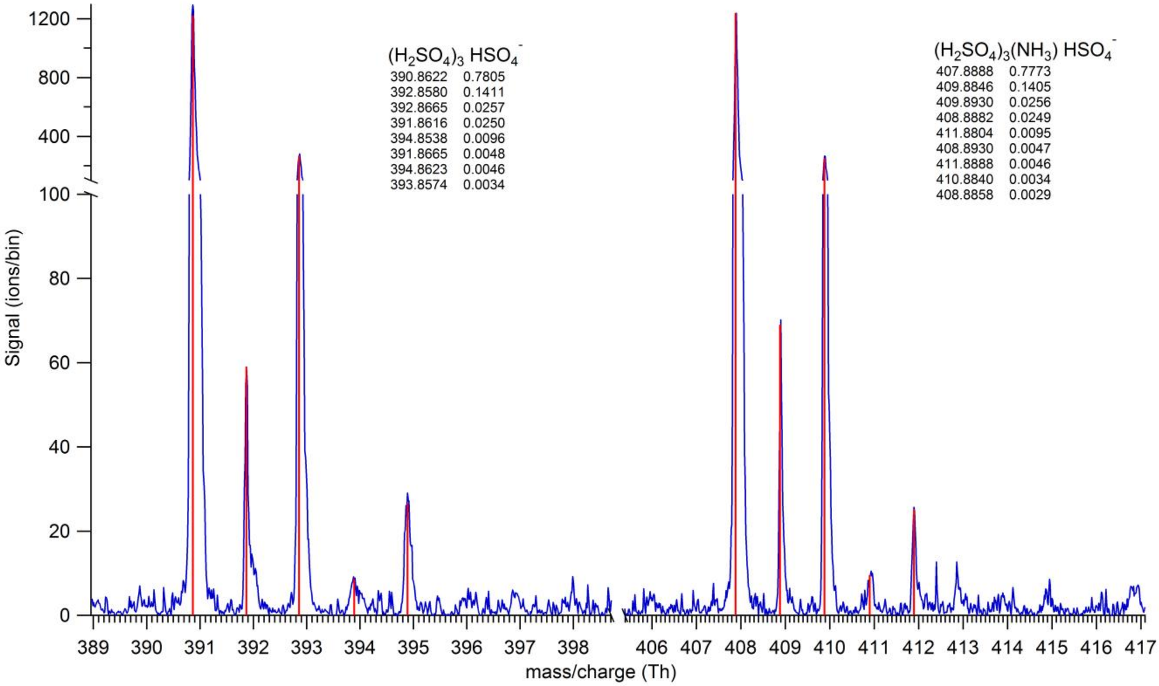

Figure S1 Example of peak fitting of $(H_2SO_4)_3HSO_4^-$ and $(H_2SO_4)_3(NH_3)HSO_4^-$ and their corresponding isotopes. The notation below each molecular formula shows the mass and abundance of the main isotopes.

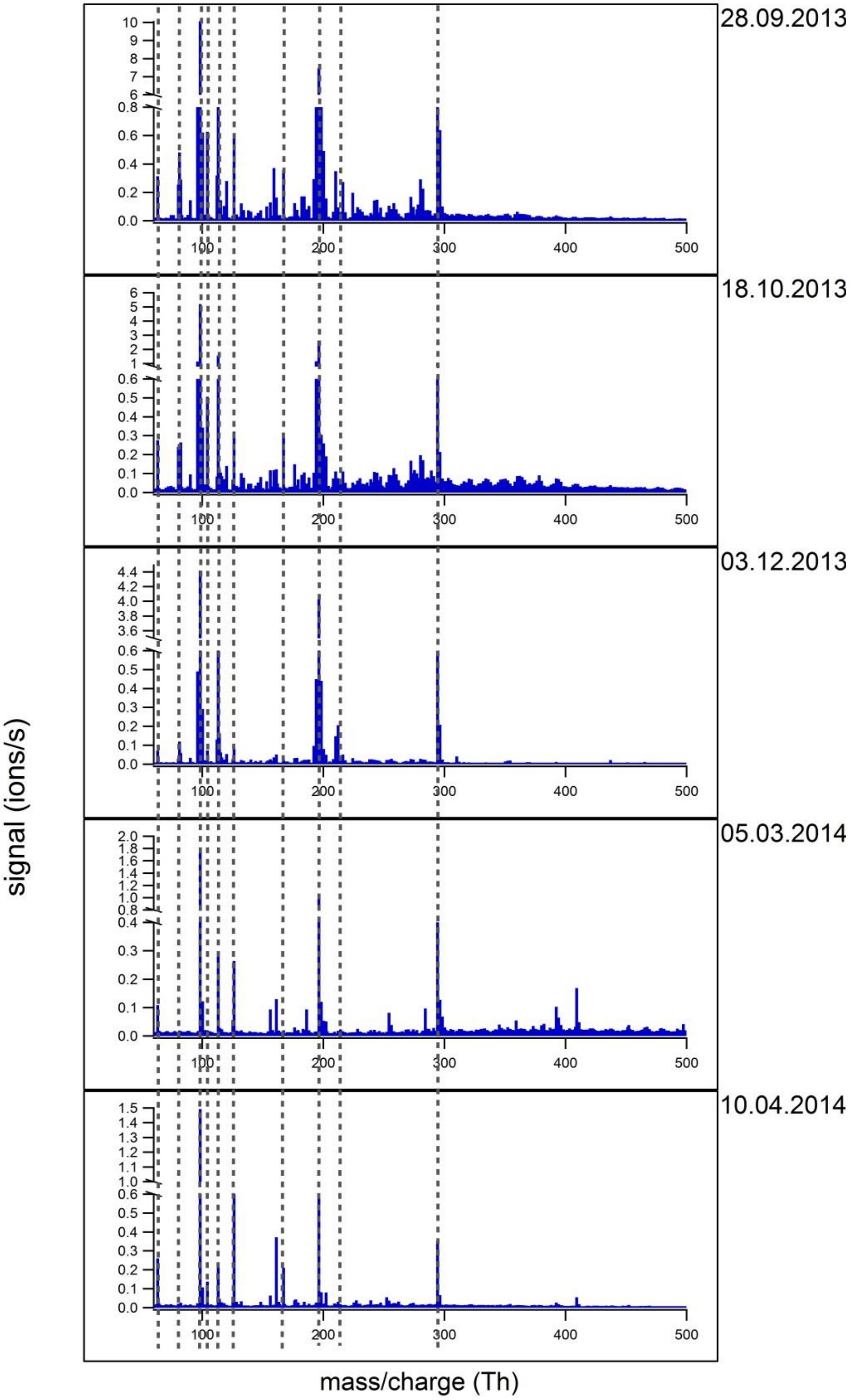

Figure S-2. Comparison of spectra in different months. Dotted lines show the main peaks as constant independently of the season.