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 R1 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.

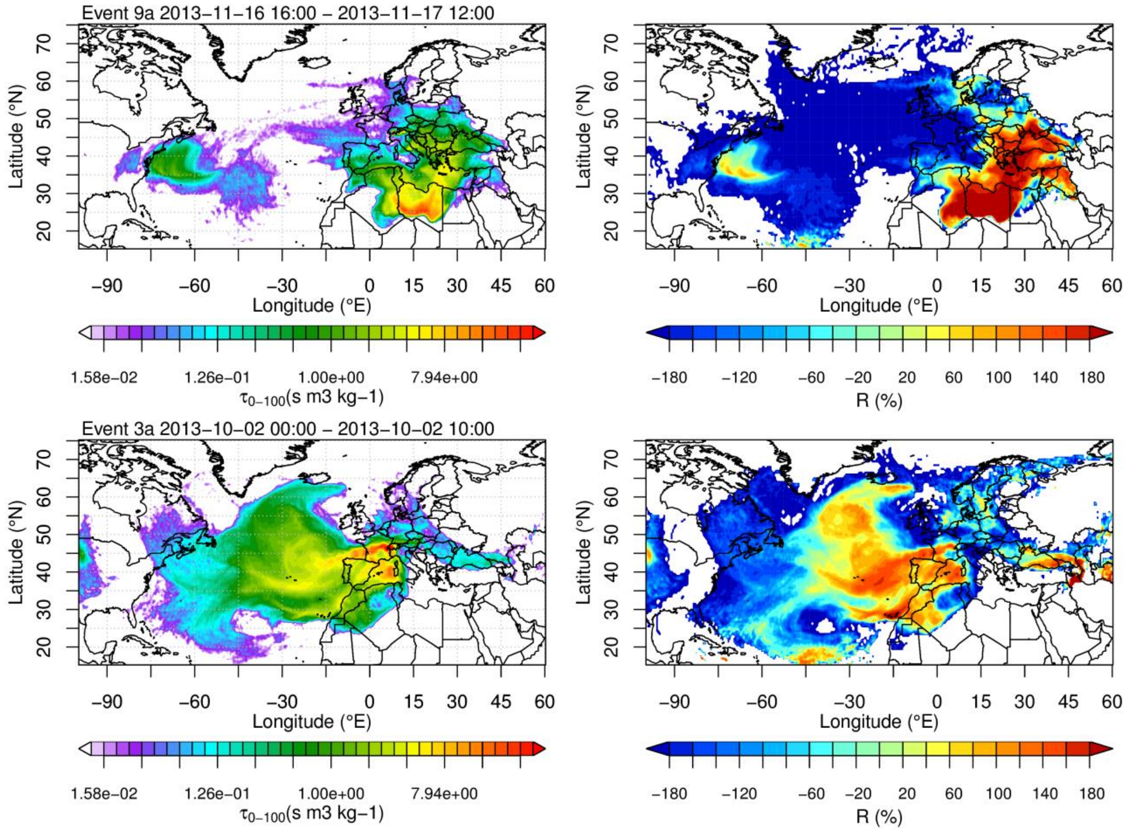

Figure R1. Recalculated relative footprint by dividing the halogen ion event footprints by the mean over all the days where a high ion signal was measured (TIC ≥ 20 cps).

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 R2 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.

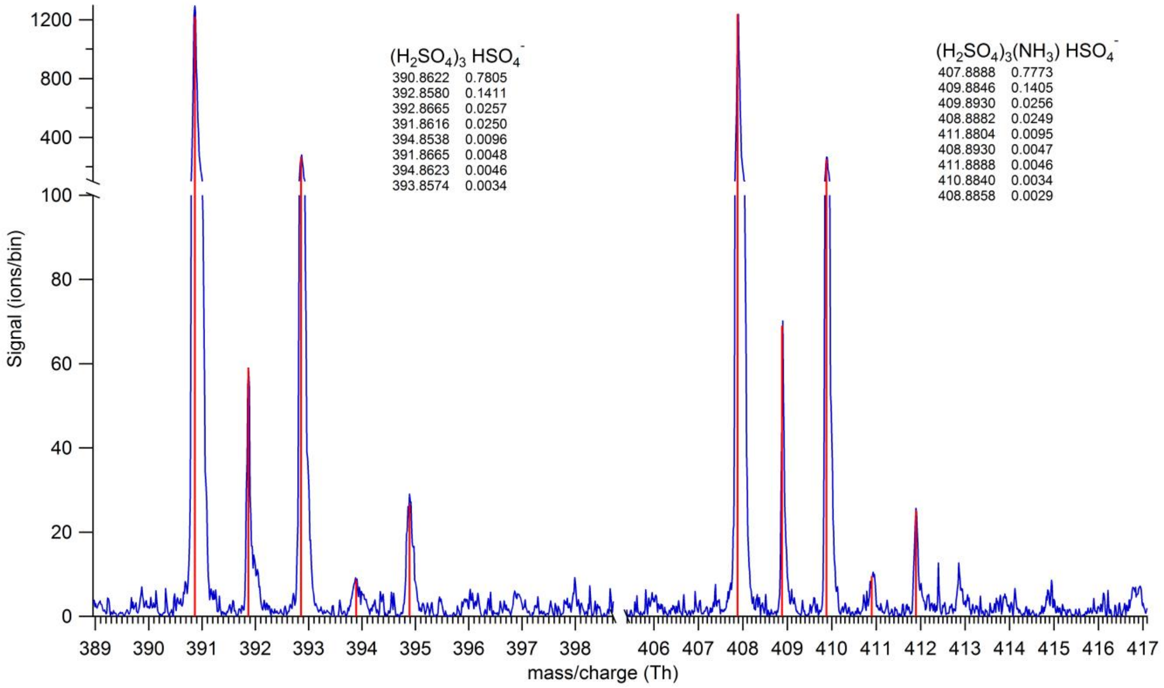

Figure R2. Fitting of (H2SO4)$_3$HSO$_4^-$ and $(H_2SO_4)_3(NH_3)HSO_4^-$ and their corresponding isotopes as example of the assignment of the elemental composition.

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 R3 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.

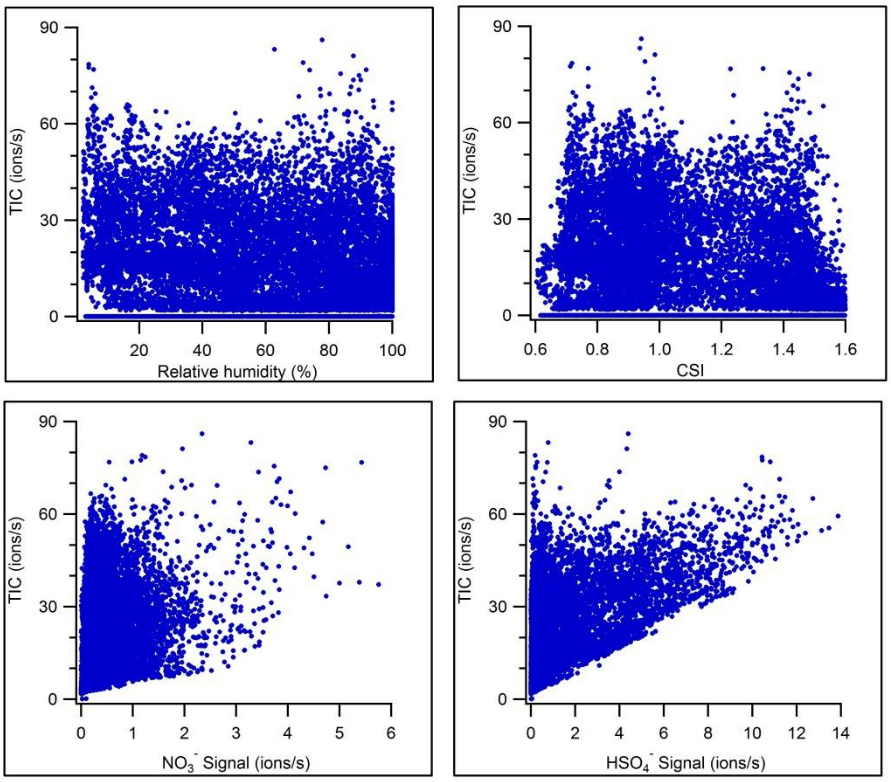

Figure R3. Scatter plots of the TIC against the cloud coverage (CSI) and the relative humidity (upper panels) and NO_3^- and HSO_4^- signals (lower panels).

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.