

## Comments Referee #3

This paper reports field measurements of atmospheric ions over a nine month period in the free troposphere at Jungfrauoch, 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 R1 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.

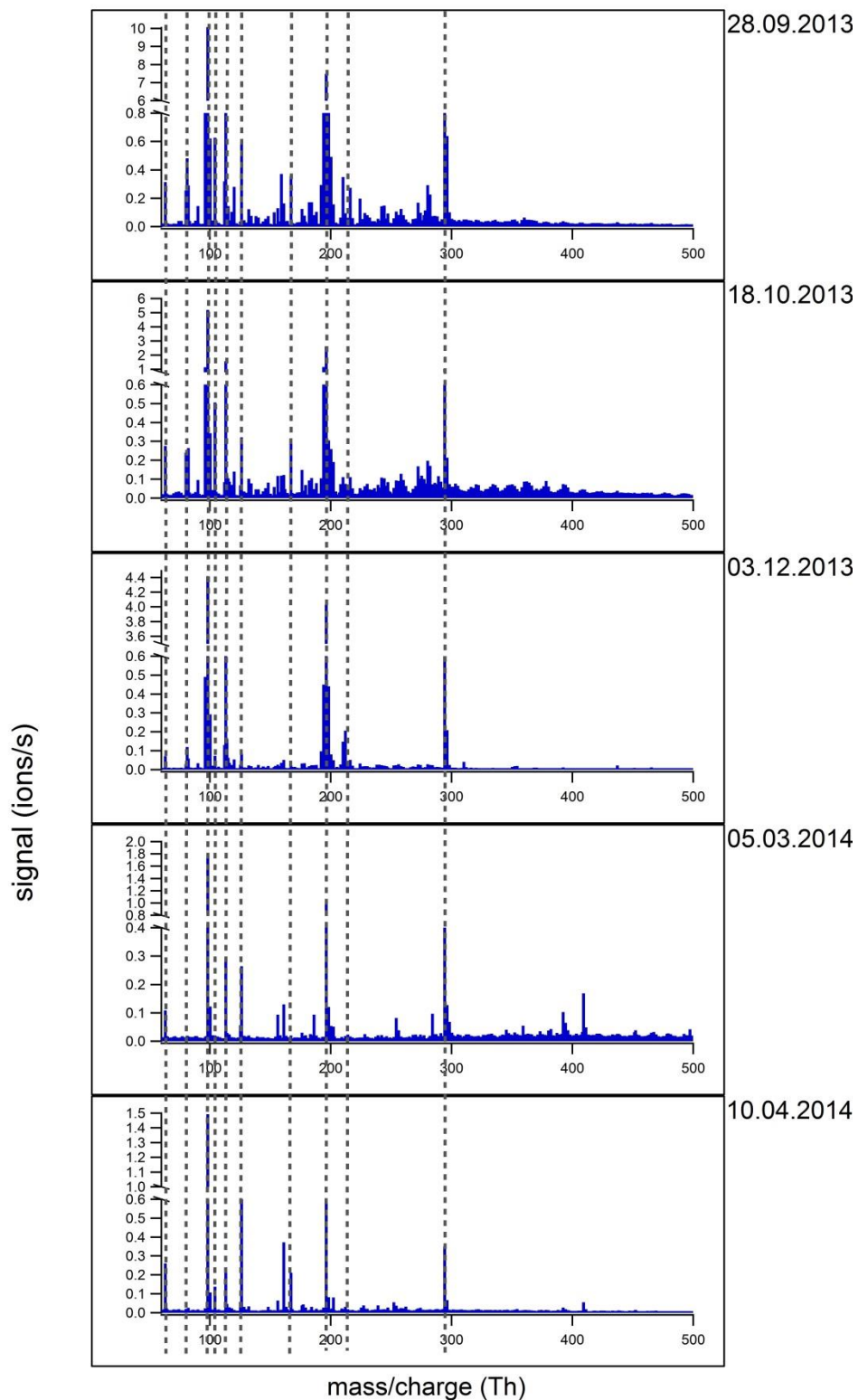


Figure R1. Spectrum of some of the averaged days corresponding to different months. No substantial seasonal variation is observed in the composition of the main ions.

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 Fig S.2.

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.

$\text{HSO}_4^-$  is most probably formed by an acid base reaction of sulfuric acid with an ion. The diurnal cycle of  $\text{HSO}_4^-$  is a clear indication that it follows the sulfuric acid concentration. In Fig.4 we presented a mass defect plot showing not only  $\text{HSO}_4^-$  but also its clusters,  $(\text{H}_2\text{SO}_4)_{1-3}\text{HSO}_4^-$ . 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  $\text{HSO}_4^-$  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  $(\text{H}_2\text{SO}_4)_{1-3}\text{HSO}_4^-$  or  $(\text{CH}_3\text{SO}_3\text{H})_{1-3}\text{CH}_3\text{SO}_3^-$  (shown in Figure 4) 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.  $\text{C}_5\text{H}_6\text{O}_6\text{NO}_3^-$ ). 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  $\text{SO}_5^-$ . In fact, Eisele et al., (JGR, 111, D04305, 2006) mentioned how this ion was produced in the atmosphere.

Experimental reports of  $\text{SO}_5^-$  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  $\text{SO}_5^-$  reports from ambient measurements. Eisele et al. (2006) speculated about  $\text{SO}_5^-$  formation as an explanation to the dip of  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  in their measurements. The authors compared their ion measurements with model predictions and based on experimental studies about  $\text{SO}_5^-$  formation

by Mohler et al. (1992), they suggested  $\text{SO}_5^-$  formation as possible explanation for a redistribution of charge in the sampled molecules under high  $\text{SO}_2$  levels. However, the authors do not show or mention ambient measurements of  $\text{SO}_5^-$ .

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  $\text{SO}_5^-$  and the authors need to provide some clarification

Can the reviewer specify which is the contradiction?

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