## Reply to Referee #2

We thank Anonymous Referee #2 for their helpful and constructive comments. We have answered to the comments below. Bold text is quoted from the referee's comments, and the text in italics has been added to the manuscript. The changes are also highlighted in the revised manuscript. Note that the numbers of pages, lines, and figures in the answers refer to those in the ACPD version, not in the revised manuscript.

**GENERAL COMMENTS**

**(a) I agree with the authors that ion-induced nucleation (IIN) plays only a minor role for the conditions of the present study. However, in my opinion the authors should further emphasize that IIN seems to starts earlier compared to the neutral nucleation (see e.g. lower left panel in Figure 5). In this respect some discussion about the consequences that can be derived from this observation would be important. One conclusion could be that the charged clusters are more stable and require lower concentrations of other compounds for their growth. This could then indicate that at other sites, where the concentrations of these compounds are low, IIN could be more important.**

We modified the paragraph discussing the earlier formation of charger than neutral clusters according to the referee's suggestion. This paragraph now reads (page 33093, line 13):

*This is caused by the fact that the concentration of ions in the size bin of 1.8–3 nm started to increase earlier on NPF event days than the concentration of neutral clusters in the same size bin (Fig. 6). The earlier formation of charged than neutral clusters has previously been observed at several European measurement sites (Manninen et al., 2010; Gonser et al., 2014). One possible explanation for this is the enhancement of activation of clusters in the presence of charge (e.g. Yu and Turco, 2000; Winkler et al., 2008), which allows the charged clusters to activate earlier than the neutral clusters when the concentration of low-volatile vapors increases in the morning. This may indicate that the ion-mediated nucleation pathways could be more significant in the conditions with low precursors vapor concentrations.*

**(b) Regarding the sub-3 nm particles/clusters it would be interesting to know whether these can be regarded thermodynamically stable, or not? In other words at what size are the clusters considered to be stable particles? In previous publications written by some of the authors listed in the present publication new particle formation rates were e.g. derived for a size of 1.5 nm. Can it therefore be generally said that all particles are stable above a size of 1.5 nm which would then include the clusters relevant for this study?**

The size at which the clusters are stable, i.e. more likely to grow than decay, may depend on environmental conditions, and therefore the limit of 1.5 nm is not necessarily always valid. For determining the size range at which the clusters are stable would require detailed information on, for example, the size dependent growth rates of clusters (see Kulmala et al., 2013). This is unfortunately not available from the measurements analyzed in this study.

**(c) It is surprising to see that the sub-3 nm cluster formation seems to be a continuous process (Figure 7), which occurs also during the night and even on a day which is classified as a nonevent day (formation rate of 2 nm clusters between 0.1 and 3 $cm^{-3}$ $s^{-1}$, see page 33093, line 22/23). If this is the case it would mean that the importance of sulfuric acid might be overestimated**

**because it is not present at high concentrations during the night. Instead other compounds could be important which additionally follow the photochemical production of sulfuric acid during the day.**
As pointed out by the referee, our results indicate that the clusters are formed also at night, in the absence of the photochemical production of sulfuric acid. This is discussed in the end of the Sect. 3.4 (page 33094, line 17): “Thus, the formation of the smallest clusters seems to occur also without solar radiation, which indicates that they may be formed, for example, by the low-volatile vapors produced in the ozonolysis of organic vapors (Ehn et al., 2014; Jokinen et al., 2014). “ In addition, to further emphasize the role of other compounds besides sulfuric acid, we now added the following sentence to the conclusions (Sect. 4):
*On the other hand, it is likely that other compounds, e.g. low-volatile organic vapors, also participate in the formation of clusters.*

**MINOR COMMENTS**

**(1) Page 33080, line 17: add “a” before “minor contribution”**
We did this.

**(2) Page 33080, line 24: replace “in the” by “under”**
We did this.

**(3) Page 33082, line 16: add “the” before “sulfuric acid”**
We did this.

**(4) Page 33083, line 16 (or in section 2.1): please mention the size range of the DMPS and also state over what size range the condensation sink was calculated**
We modified the sentence to include also the upper size limit of the DMPS measurements. We also added a reference to Laaksonen et al. (2005) where this particular DMPS system is described (page 33083, line 16):
*In addition, a twin-DMPS (Differential Mobility Particle Sizer) system was used to measure the number size distribution of particles in the size range of 3–600 nm (Aalto et al., 2001; Laaksonen et al., 2005).*
Correspondingly, condensation sink was calculated for the size range of 3–600 nm.

**(5) Page 33085, line 18: In how far is the growth rate (GR) calculated from the positive ion size distribution representative for the GR of the neutral particles? Especially for the smallest size range (1.5 to 3 nm) the charged particles probably grow faster due to ion-dipole interactions compared to neutral-neutral collisions for the uncharged particles. Has this effect been taken into account?**
It is true that the growth rates of charged and neutral particles may differ from each other. However, in this study we were not able to determine the growth rates of neutral sub-3nm particles due to the limited size resolution of our measurements. Thus, when calculating particle formation rates we assumed that the growth rates of neutral and charged particles are equal, not taking into account the enhancement effect of charge. We are aware that this introduces additional uncertainty in our

calculations. To state this more clearly in the manuscript, we now added a following sentence in the end of Sect. 2.3 (page 33086, line 10);

*However, it needs to be noted that the growth rates of neutral and charged clusters may not be equal in reality, as the presence of charge may enhance the growth of particles (e.g. Yu and Turco, 2000; Nadykto and Yu, 2003).*

**(6) Page 33086, section 2.4: For what conditions was the $SA_{proxy}$ calculated? Mikkonen et al. (2011) report that only conditions where the global radiation exceeds 50 W $m^{-2}$ accurately predict the sulfuric acid concentration. Has this constraint been applied?**

Actually, Mikkonen et al. (2011) constructed their proxy for times when radiations exceeds 10 W $m^{-2}$. However, they state that the predictive ability of the proxy increases if the proxy is calculated only for times when radiation exceeds 50 W $m^{-2}$. In this work, we calculated $SA_{proxy}$ for moments when radiation was higher than zero. However, as pointed out by the referee, it is reasonable to use a higher limit. Therefore, we now calculated $SA_{proxy}$ only for times when radiation was higher than 10 W $m^{-2}$, as was done also by Mikkonen et al. (2011). We decided not to apply the higher threshold of 50 W $m^{-2}$, as in that case too much data from the morning and evening would be disregarded. All the results are now updated accordingly, although the changes caused by the new threshold of 10 W $m^{-2}$ are very minimal. In addition, a following sentence was added to Sect. 2.4 (page 33086, line 20):

*The proxy was calculated only for times when global radiation exceeded 10 W $m^{-2}$.*

**(7) Page 33087, line 4: please specify the meaning of "FNL"**

We added the explanation.

**(8) Page 33087, line 18: do the authors mean "compared" instead of "respect"?**

We changed "respect" to "compared".

**(9) Page 33088, section 3.1: It is not clear in how far the NPF event day and the non-event day differ in their conditions. Obviously the conditions are different in the afternoon but this is not the important time for new particle formation. In the morning (around 7 a.m.) the conditions from Fig. 1 seem to be quite similar for the NPF event days and the non-event day. In this respect it also not evident in how far the parameters shown in Fig. 1 reflect the results by Sogacheva et al. (2007) meaning that stronger mixing in the PBL favors NPF. Maybe other meteorological parameters (e.g. wind speed) can support the statement.**

We now modified Fig. 1 so that the conditions on NPF event days and the non-event day can be more easily compared. In addition, 25% to 75% percentile ranges of different variables are presented for NPF event days. Although the difference between NPF event days and the non-event day can be most easily noticed in the afternoon, the conditions differ also in the morning. In the morning of the non-event day, radiation is lower, and condensation sink and RH are higher than typically at the same time on event days. However, it is true that there is no clear difference in the development of boundary layer in the morning of event days and the non-event day. Therefore, we removed the sentence where it was stated that the results are in the agreement with Sogacheva et al. (2007).

**(10) Page 33091, line 7 to 9: Something is missing in this explanation. The longer measurement time cannot be solely responsible for the slower median growth rate.**
As the referee found our explanation unsolid, we checked the growth rate data of the study by Manninen et al. (2010). It seems that during their measurement period extending from March to September, it was possible to determine the growth rate in the sub-3nm size range only for 7 NPF events. Of those 7 events, 5 took place in spring (March-April) and only 2 in summer. Thus, the lower value of growth rate in their study may be due to the fact that in spring the production of condensable vapors is likely lower than in summer. Thus, we modified the sentence in the following way (page 33091, line 7):
*The lower value of median growth rate compared to our results is likely caused by the fact that the most of the events for which Manninen et al. (2010) were able to determine the sub-3nm growth rate occurred in spring, when the production of condensable vapors is typically lower than in summer time.*

**(11) Page 33092, line 10 and 11: Do these numbers include the effect of ion-ion recombination? If not, the authors should also provide the numbers if this effect is included.**
No, we did not take into account the effect of ion-ion recombination here, but we agree that it should be done to obtain the total fraction of clusters formed by ion-mediated pathways. Thus, we now calculated the ion-mediated nucleation fraction by including also ion-ion recombination, and added the following sentence (page 33902, line 11):
*When the contribution of ion-ion recombination is also taken into account, the total ion-mediated nucleation fraction becomes 0.8% at 1.6 nm and 3.7% at 2 nm*.

**(12) Page 33094, line 9: replace “nigh-times” by “night-time”**
We did this.

**(13) Page 33095, line 1: It is mentioned here that the SO2 concentrations were observed to be higher on NPF days than on non-event days (Hamed et al., 2007). Is this the case here also?**
Yes, $SO_2$ concentration was on average higher on event days than on the non-event day. As this is a rather relevant result, we added the median diurnal pattern of $SO_2$, as well as $SA_{proxy}$, to Fig. 1, and then also added a paragraph in Sect. 3.1 describing them. Furthermore, we also now specify the model of $SO_2$ monitor in Sect. 2.1, where instrumentation is described.

**(14) Page 33116, Figure 7: the figure legend is too small**
We increased the size of the legend.

**(15) Page 33117, Figure 8: In an earlier comment it was pointed out that the $SA_{proxy}$ should only yield accurate results when the global radiation exceeds 50 W $m_{-2}$ which is the case only during day time. The color code suggests that the $SA_{proxy}$ was calculated for a full day (24 h). How is this possible? In addition, the sulfuric acid concentration should be shown on a log-scale to avoid hiding the low values.**
As explained in the answer of the comment (6), the proxy was now calculated only for times when global radiation exceeds 10 W $m^{-2}$. In this case, the earliest moments for which $SA_{proxy}$ was calculated

were around 4 a.m., and the latest moments were around 8 p.m. (UTC + 1h). The color bar shown in the figure covers the full day, as we wanted to have the same color scale in the Figs 7 and 8.

We changed the x-axis in Fig. 8 to a logarithmic scale, as suggested by the referee. To be consistent, we also changed the x-axis to a logarithmic scale in Fig. 9. We also now calculated correlation coefficients between cluster concentrations and CS and sulfuric acid proxy by using logarithmic values of all the variables, which changes the values slightly. We modified the paragraphs discussing the correlations accordingly.