Reply to Referee #1

We thank Anonymous Referee #1 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

The paper by Kontkanen et al. discusses the concentrations of neutral and charged sub-3nm clusters measured at the San Pietro Capofiume station, in the framework of the PEGASOS campaign. This study focuses on the connection between these small clusters and the occurrence of new particle formation (NPF) process. The conditions that could favor the NPF process are also investigated, including meteorological parameters as well as sources and sinks for the gaseous precursors, coupled with boundary layer height and air mass backtrajectories.

I recommend the publication of this paper as it provides new measurements of sub-2nm neutral clusters at the San Pietro Capofiume station, which are a complement to the previous studies focusing on small clusters and NPF conducted at the station (Hamed et al., 2007; Sogacheva et al., 2007). Such observations remain rare in the literature and are of great interest to improve our understanding of the NPF process. However, I have several comments and recommendations that are listed below and should be addressed in a revised version. As a global comment, since the comparison between event and non-event days only include one non-event day, I would suggest 1) to provide the variability associated to median values as often as possible in order to evaluate if the differences observed between this day and the others is significant and 2) to provide more balanced conclusions.

The variability of different variables in addition to the median diurnal pattern is now provided, as suggested by the referee (see the answer to the comment P33087, Section 3.1). We also improved Sect. 4, where the conclusions are presented.

SPECIFIC COMMENTS

P33081, l22-25: I believe that in order to complete the general statement regarding the impact of the background aerosol concentration on the NPF process, a short additional discussion should be proposed to underline the fact that the role of the condensation sink can be much more complicated than suggested here. In fact, if the condensation sink is on average lower on event days compared to non-event days at boundary layer (BL) stations, the opposite is observed at high altitude sites (Manninen et al., 2010). Moreover, in Section 3.3 of the present study, the authors highlight the fact that at BL stations, increased pollution levels could favor higher cluster formation rates.

It is true that the conditions favoring NPF may not be similar at high-altitude sites as in the boundary layer. Thus, we modified the text to make it clear that we refer here to the observations made in the boundary layer. The sentence now reads (page 33081, lines 22–25):

In addition, NPF has been observed to be more favorable in the boundary layer when relative humidity and background aerosol concentrations are low (Hyvönen et al., 2005; Hamed et al., 2011; Nieminen et al., 2015).

Also, we want to point out that earlier on the same page (page 33081, lines 8–9) we also mention that the anthropogenic emissions of SO_2 may favor the formation of clusters.

P33083, l8-26: If the accuracy of NAIS and DMPS measurements has been widely discussed in previous studies and is now quite well known, the accuracy of the PSM, which is much more recent compared to the other instruments, should be briefly discussed here. In particular the authors should discuss the uncertainties related to the charging state and to the chemical composition of the clusters (Kangasluoma et al., 2013; Wimmer et al., 2013).
We agree that adding some discussion about the uncertainties related to the determination of the PSM cut-off sizes would be useful. Therefore, we added the following sentences and references to the manuscript (page 33083, line 15):
These cut-off sizes were determined based on laboratory calibrations using ammonium sulphate particles produced in a tube furnace. It needs to noted, though, that the cut-off size of the PSM has been observed to depend on environmental conditions, especially on relative humidity, and on the composition and the charge of clusters (Kangasluoma et al., 2013; Wimmer et al., 2013). Therefore, the cut-off sizes obtained in the laboratory may not correspond exactly to the cut-off sizes of the instrument in field measurements.
We want to point out that as the concentration of sulfuric acid is relatively high in San Pietro Capofiume, using ammonium sulphate particles for calibrating the PSM is plausible.

P33087, l10-11: Don't you think that focusing on the last 24 hours of the back trajectory can be misleading for a study dedicated to sub-3 nm clusters since it has been reported by Tunved et al. (2005) that the turnover time of these small clusters is longer, around 1.6 – 1.7 days?
Actually, the turnover time for sub-3nm, and particularly for sub-2nm clusters, is much shorter; Tunved et al. (2005) considered in their study NPF events with the growth of particles from 3 nm to 25 nm. On the other hand, it is true that the precursor gases (e.g. SO_2) may have a longer lifetime than 24 h. However, we think that using the time period of 24 h is plausible regarding our data analysis method. To determine the arrival direction of air mass, we used the following criterion: a trajectory had to spend over 70% of the last 24 h before arriving to San Pietro Capofiume in a certain sector. Thus, if the studied time period would be clearly longer than 24 h, the determination of the arrival direction would be more difficult as the trajectory would not as likely stay inside a certain sector most of that time.

P33087, Section 3.1: The robustness of the comparison between event and non-event days which is proposed in this section could be debated since there is only one non-event day included in the analysis. In order to give more sense to this comparison, I would suggest to indicate the variability of the measurements on event days. This information is crucial to evaluate if the PBL height significantly increases on the non-event day compared to event days (P33088, l23-24), and also if the CS is significantly lower in the first part of the nonevent day compared to event days (P33089, l11-12).
To make the comparison between event days and the only non-event day more robust, we now modified Fig. 1 so that in addition to the median diurnal pattern, 25% to 75% percentile ranges are presented for event days. In addition, in Fig. 1 the diurnal pattern of a certain variable on event days and on the non-event day are now in the same figure, which makes comparing them easier. We also

added the diurnal patterns of SO_2 and SA_{proxy} in the figure. The section 3.1 was modified to correspond to the new figure.

P33089, Section 3.2: I would suggest to merge this section with Section 3.4 since they both deal with small clusters concentration.

We thank the referee for this suggestion. However, we still think that the structure of the manuscript is logical in its current form. Now the Sect. 3.2 first gives an overview of the observed cluster concentrations. In Sect. 3.3 new particle formation is discussed, including the median values of the growth rates and formation rates. Then in Sect. 3.4 we focus on the diurnal variation of cluster concentrations and particle formation rates.

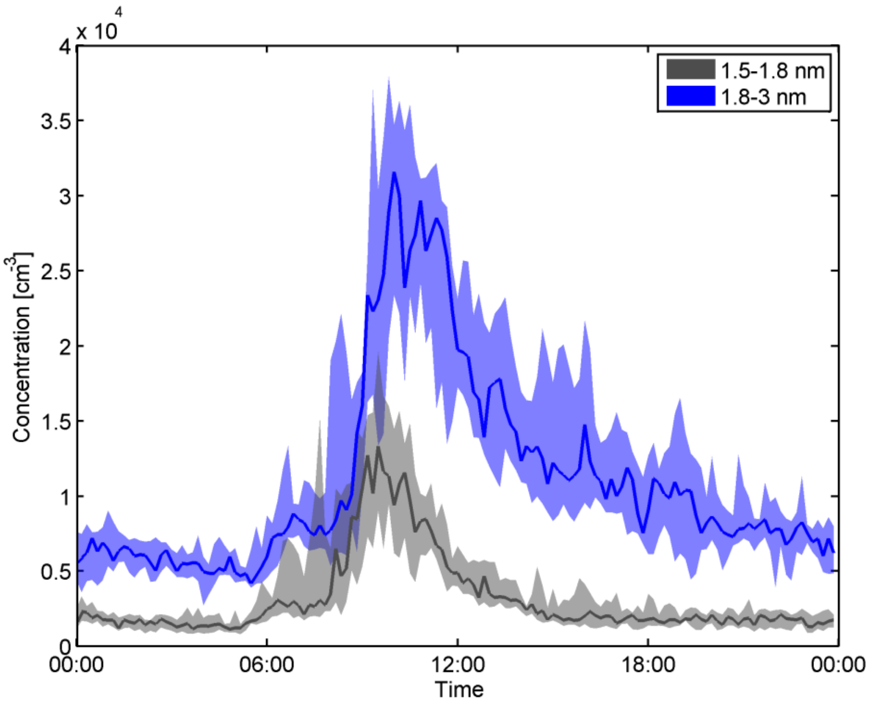
P33091, l21: Was the CS discussed in this section and in Section 3.5 calculated using "wet diameters"? The impact of the hygroscopic growth of particles was previously shown to be significant in the CS calculation (Laakso et al., 2004).

Yes, the effect of hygroscopic growth was taken into account. To make this clear, we modified the sentence explaining how CS is calculated (page 33086, line 20):

CS is the condensation sink that we calculated from the particle size distributions measured with the DMPS assuming that the condensing vapor is sulfuric acid, and correcting for the hygroscopic growth of particles (Kulmala et al., 2001; Laakso et al., 2004).

P33092, l24-25: Although I agree with the fact that based on Fig 5 the median cluster concentration in the size range 1.5-1.8 nm reaches its maximum slightly before the one of larger clusters, I wonder if this shift remains significant when considering the variability of the measurements.

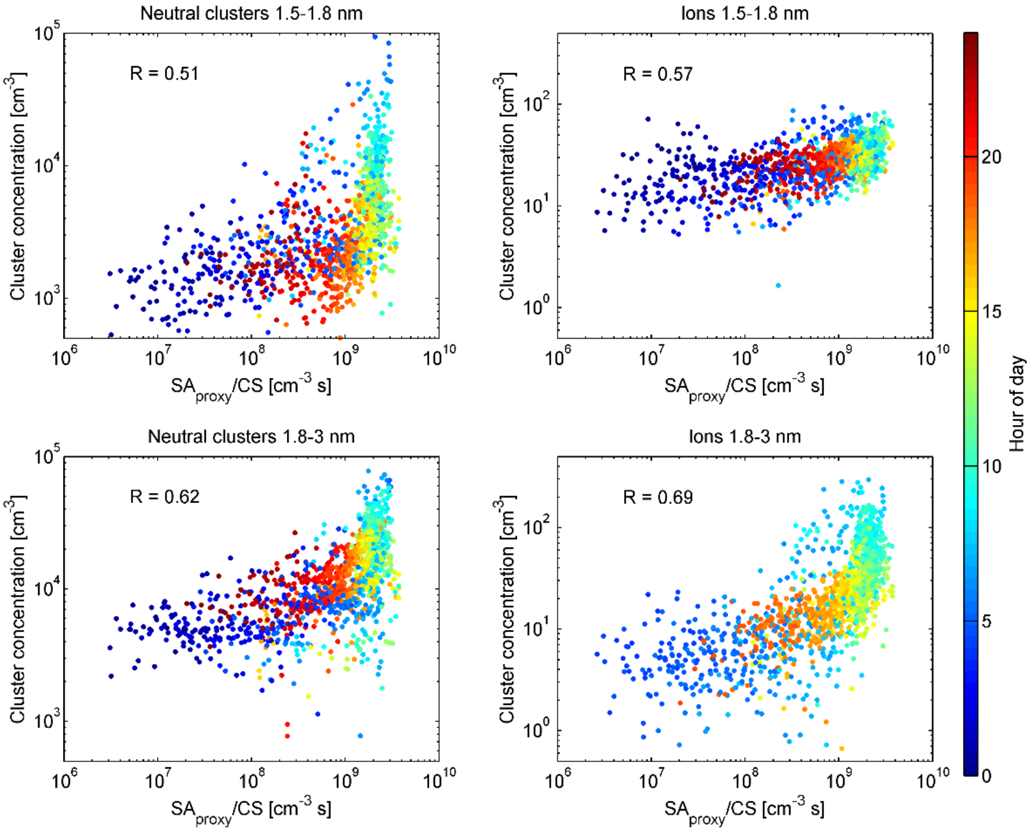
To investigate this, we plotted the median and 25% to 75% percentile range of the diurnal patterns for these two size ranges (see figure below).



From the figure we can see that the maximum in the size bin of 1.8–3 nm occurs later than the maximum in the size bin of 1.5–1.8 nm. However, it is true that this time difference is not so clear when studying times at which the concentration reaches the maximum, while it becomes obvious when times at which the concentration starts to decrease again are studied. Therefore, we modified the sentence slightly; it now reads (page 33092, line 24):
The concentration maximum occurred slightly earlier in the size bin of 1.5–1.8 nm than in the larger, 1.8–3 nm, size bin.

P33093, l24-27: Based on the median values shown on Fig. 7, the formation rate of 2 nm negative clusters reaches higher values compared to the formation rate of 1.6 nm clusters of the same polarity. This observation is quite unexpected since the formation rate typically decreases with particle size because of the coagulation process. Do the authors have an explication for that?
We thank the referee for pointing this out. We investigated this issue and found that the low formation rate of negative ions at 1.6 nm is caused by the fact that during the campaign the sensitivity of the NAIS for 1.5–1.8 nm negative ions was lowered due to electrometer noise level in these channels. This can also be seen when comparing the concentrations of negative and positive 1.5–1.8 nm ions. For example, Fig. 2 shows that the concentration of negative ions is lower than the concentration of positive ions in the 1.5–1.8 nm size range. To make this clear, we added a following sentence (page 33089, line 26):
The observed lower concentration of negative 1.5–1.8 nm ions compared to positive ions is mainly caused by the lower sensitivity of the negative polarity of NAIS to detect these ions, which results from slightly higher electrometer noise levels in corresponding channels.
In addition, we added the following sentence to explain the relatively low formation rate of 1.6 nm negative ions (page 33092, line 7):
Note that the lower formation rate of 1.6 nm negative ions than positive ions in our measurements is mainly due to the lowered sensitivity of negative polarity of the NAIS to detect 1.5–1.8 nm ions.

P33094, Sections 3.5 and 3.6: Regarding the effect of CS and sulfuric acid. As suggested by the authors, the sources and sinks for NPF could share the same origin. It is thus not surprising to observe a correlation between the cluster concentration and the sulfuric acid concentration, and no clear anti-correlation between the cluster concentration and the CS. I clearly believe that it would be more relevant to consider these two parameters simultaneously in the form of a ratio H2SO4/CS, which could for example indicate is the NPF process is favored when the source is dominant compared to the sink (high ratio).
As the referee suggested, we studied the correlation between cluster concentrations and the ratio of sulfuric acid proxy to condensation sink. The figure below shows the obtained results:



As can be seen from the figure, the correlation coefficients obtained between cluster concentrations and SA_{proxy}/CS are close to the correlation coefficients obtained for only SA_{proxy} being slightly lower for neutral cluster and slightly higher for ions. Thus, we think that adding this figure to the manuscript is not necessary. However, we added a sentence explaining this result in the end of Sect. 3.5 (page 33095, line 24):

We also investigated the correlation between the cluster concentrations and the ratio of the sulfuric acid proxy to condensation sink. The correlation coefficients obtained between this ratio and the neutral cluster concentrations were slightly lower than between neutral clusters and only sulfuric acid (R = 0.51 in the size bin of 1.5–1.8 nm, and R = 0.62 in the size bin of 1.8–3 nm). On the other hand, for ions the correlation coefficients were slightly higher in this case (R = 0.57 in the size bin of 1.5–1.8 nm, and R = 0.69 in the size bin of 1.8–3 nm).

P33095, l7-9: How can you justify that the correlation which is observed between sulfuric acid and the cluster concentration on Fig. 8 clearly express a decisive involvement of H2SO4 in the NPF process? Don't you think that this correlation could also be explained by the fact that both the formation of sulfuric acid and clusters is a diurnal process? I believe that such correlation would also be observed with other oxidized organic compounds, which are produced through photochemical processes. In order to really assess the role of sulfuric acid and justify that it is "essential for cluster formation", I trust that it would be necessary to follow other compounds and to have information on the cluster chemical composition, using instruments such as the Api-Tof.

We agree that the correlation between sulfuric acid and cluster concentration does not prove that sulfuric acid is essential for the cluster formation, and therefore we modified the sentence the referee is referring to (page 33095, line 7):
In agreement with earlier studies, the sub-3nm cluster concentrations correlated positively with sulfuric acid proxy indicating that sulfuric acid possibly participates in the cluster formation in San Pietro Capofiume (Fig. 8).

P33095, Section 3.6: I would suggest to add a map in the background of Fig. 10 in order to ease the understanding of the explanations that are provided at the end of the section. Also, since the cluster formation rate was found to be maximum around 9:00 pm, is it relevant to investigate the connection between cluster concentration, NPF, sulfuric acid and CS focusing on air masses that reach the station between 10 a.m. and 2 p.m., i.e. partially after the nucleation peak?
We did not add a map in the Fig. 10 to keep the figure simple, but we added a map in the Sect. 2.1 where the measurement site is described.
The time window between 10 a.m. and 2 p.m. was selected for the trajectory analysis, as we wanted to investigate the effect of the general meteorological situation on the cluster formation, and not focus only on the morning time with thin, still developing boundary layer. However, even if the time window would have been selected for example from 9 a.m. to 1 p.m., the results would not likely change significantly.