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.

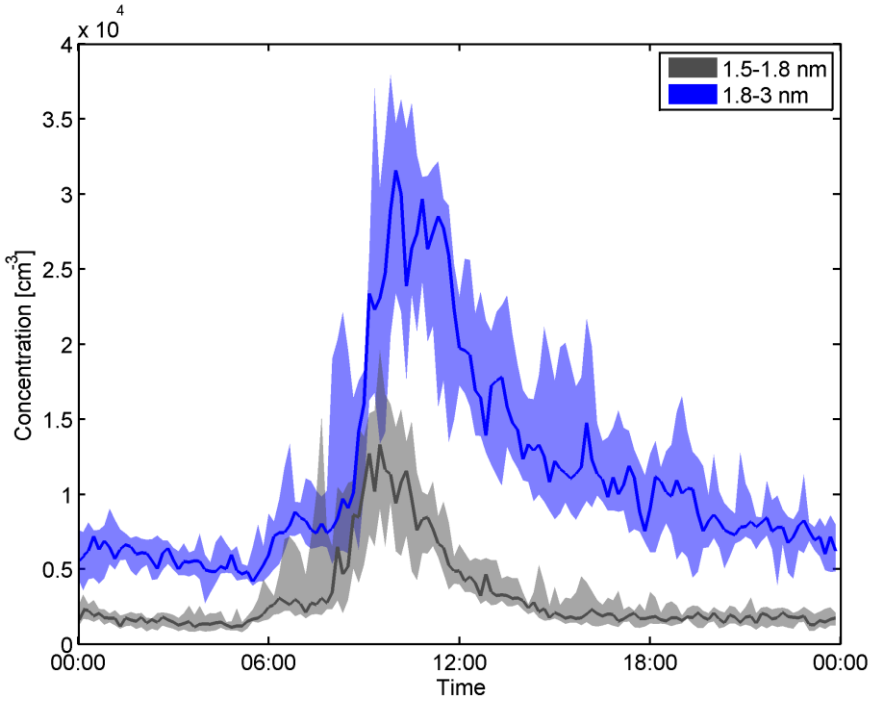
P33091, l21: Was the CS discussed in this section and in Section 3.5 calculated using "wet diameters"? The impact of the hygroscopic growth of particles was previously shown to be significant in the CS calculation (Laakso et al., 2004).

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.

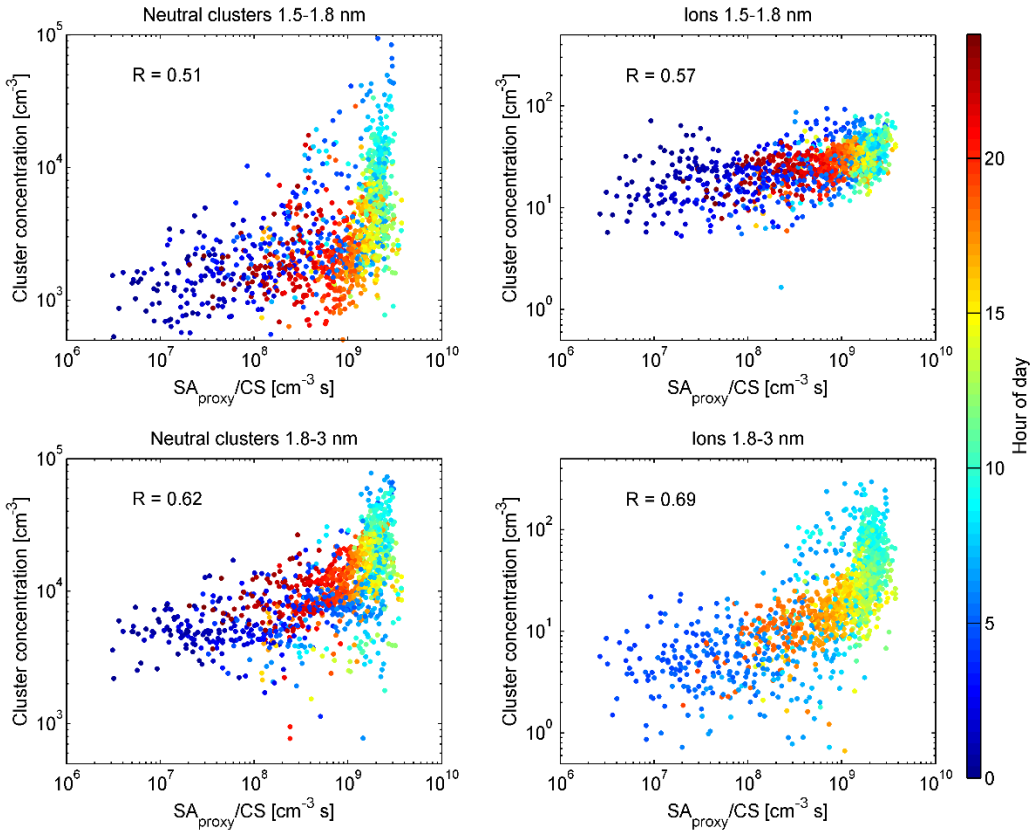
To investigate this, we plotted the median and 25% to 75% percentile range of the diurnal patterns for these two size ranges (see figure below).



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.

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.

High concentrations of sub-3nm clusters and frequent new particle formation observed in the Po Valley, Italy, during the PEGASOS 2012 campaign

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Abstract

The concentrations of neutral and charged sub-3nm clusters and their connection to new particle formation (NPF) were investigated during the PEGASOS campaign (7 June – 9 July, 2012) at the San Pietro Capofiume measurement station in the Po Valley, Italy. Continuous high concentrations of sub-3nm clusters were detected during the measurement period, although the condensation sink was relatively high (median value 1.1×10^{-2} s^{-1}). The median cluster concentrations were 2140 cm^{-3} and 7980 cm^{-3} in the size bins of 1.5–1.8 nm and 1.8–3 nm, and the majority of them were electrically neutral. NPF events were observed during the measurement period frequently, on 86% of the days. The median growth rates of clusters during the events were 4.3 nm h^{-1}, 6.0 nm h^{-1} and 7.2 nm h^{-1} in the size ranges of 1.5–3 nm, 3–7 nm and 7–20 nm. The median formation rate of 1.6 nm clusters was high, 45 cm^{-3} s^{-1}, and it

exceeded the median formation rate of 2 nm clusters by one order of magnitude. The ion-induced nucleation fraction was low; the median values were 0.7% at 1.6 nm and 3.0% at 2 nm. On NPF event days the neutral cluster concentration had a maximum around 9 a.m. (local winter time), which was absent on a non-event day. The increase in the cluster concentrations in the morning coincided with the increase in the boundary layer height. At the same time radiation, temperature and SO_2 concentration increased, and RH and condensation sink decreased. The concentrations of neutral and charged clusters were observed to have a positive correlation with sulfuric acid proxy, indicating the significance of sulfuric acid for the cluster formation in San Pietro Capofiume. The condensation sink had a negative correlation with the concentration of charged clusters but no clear relation to the neutral cluster concentration. This finding, together with back-trajectory analysis, suggests that the precursor vapors of the clusters and background aerosol particles, acting as their sink, have possibly originated from the same sources, including e.g. power plants and industrial areas in the Po Valley.

1 Introduction

New particle formation (NPF) is a dominant source of aerosol particles in the atmosphere (Spracklen et al. 2006; Yu et al., 2010). The process takes place by the formation of nanometer-sized atmospheric clusters and their subsequent growth to larger particles (Kulmala et al., 2007; 2013). After that they may affect the climate through indirect radiative effects of aerosol particles (Merikanto et al., 2009; Wang and Penner, 2009; Kazil et al., 2010; Makkonen et al., 2012). NPF has been observed around the world in various locations (Kulmala et al., 2004a; Zhang et al., 2012). Although recent chamber studies have provided insight into the role of different chemical compounds in NPF (Kirkby et al., 2011; Almeida et al., 2013; Schobesberger et al. 2013; Riccobono et al., 2014), the exact mechanisms, by which the process takes place in different ambient conditions, are still unknown. The summary of the recent knowledge on physical and chemical processes behind NPF is given by Kulmala et al. (2014).

The relative importance of electrically neutral and charged clusters in atmospheric NPF has been under discussion for decades. Some model studies underline the importance of ions (Yu and Turco, 2000; Yu and Turco, 2008), while field measurements conducted with ion spectrometers suggest only a minor contribution of ions to NPF in the continental boundary layer (Iida et al., 2006; Kulmala et al., 2007; Manninen et al., 2010) and also higher in the troposphere (Mirme et al., 2010). Recent instrumental development has enabled measuring the

concentrations of sub-3nm particles also with condensation particle counters, including a Particle Size Magnifier (PSM; Vanhanen et al., 2011). With these measurement techniques, it has been observed that sub-3nm neutral clusters exist in boreal forest (Lehtipalo et al. 2009; Kulmala et al., 2013), in coastal areas (Lehtipalo et al., 2010), and at high altitude under free tropospheric conditions (Rose et al., 2015). At all these sites, the concentrations of neutral clusters clearly exceed ion concentrations during NPF, which indicates that neutral nucleation mechanisms dominate in these environments. Furthermore, high concentrations of sub-3nm clusters during NPF events have been detected with a PSM at urban sites in the United States (Yu et al., 2014) and at urban, heavily polluted, sites in China (Xiao et al., 2015; Yu et al., 2015).

In many of the earlier studies, sub-3nm clusters detected with a PSM have been observed to be associated with elevated sulfuric acid concentration (Kulmala et al., 2013; Yu et al., 2014). This indicates that sulfuric acid is a key compound in the formation of atmospheric clusters, as has been proposed already earlier (e.g. Weber et al., 1997; Sipilä et al., 2010). Sulfuric acid is formed in the atmosphere by the oxidation of sulfur dioxide (SO_2), which is largely produced in fossil fuel combustion. Therefore, anthropogenic emissions of SO_2 may enhance the formation of sub-3nm clusters. On the other hand, high aerosol surface area related to anthropogenic emissions may reduce the sub-3nm cluster concentrations by coagulation (Kerminen et al., 2001; Xiao et al., 2015). Besides sulfuric acid, organic compounds with very low volatility may participate in atmospheric cluster formation (Kulmala et al., 1998; Metzger et al., 2010; Ehn et al., 2014; Schobesberger et al., 2013; Riccobono et al., 2014). These compounds are formed in the atmosphere in the oxidation of VOCs (volatile organic compounds), mainly originating from biogenic sources, such as vegetation (Günther et al., 2012).

In addition to the concentrations of low-volatile precursor vapors, meteorological conditions may influence the sub-3nm cluster concentrations. Local meteorology can affect cluster concentrations in several ways. For instance, solar radiation drives oxidation mechanisms forming low-volatile vapors, which, as mentioned above, may participate in the formation of clusters. This is indicated by numerous observations on the importance of solar radiation for NPF (e.g. Boy et al., 2002; Nieminen et al., 2015). 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). It has

also been proposed that the beginning of NPF may be linked to the onset of turbulence in the boundary layer (Nilsson et al, 2001a). In addition, the origin of air masses has been connected to the probability of NPF events in several locations (Nilsson et al., 2001b; Sogacheva et al., 2007; Nieminen et al., 2015).

In this study, we investigated the concentrations of sub-3nm clusters at the San Pietro Capofiume station located in the Po Valley, Italy, during the PEGASOS campaign (7 June – 9 July, 2012). Previously, NPF events have been found to be frequent in San Pietro Capofiume during summer (Laaksonen et al., 2005; Hamed et al., 2007; Manninen et al., 2010), which may be due to the high emissions of anthropogenic precursor vapors and favorable meteorological conditions. Here, our aim is to further investigate NPF occurring at this site focusing on the concentrations of sub-3nm clusters and their connection to NPF events. Furthermore, we aim to elucidate the effect of meteorological conditions and the presence of anthropogenic pollutants on the sub-3nm cluster concentrations in San Pietro Capofiume. During the campaign, the concentration of all sub-3nm clusters were measured with a PSM and the concentration of charged clusters with a NAIS (Neutral cluster and Air Ion Spectrometer; Kulmala et al., 2012). From these measurements, we determined the growth rates and formation rates of clusters. We compared the diurnal variation of cluster concentrations and their formation rates to the diurnal evolution of planetary boundary layer and the variation of different meteorological variables. In addition, we studied how the sulfuric acid concentration and condensation sink as well as the origin of air masses affect the concentrations of sub-3nm clusters observed in San Pietro Capofiume.

2 Measurements and data analysis

2.1 Site description and instrumentation

The measurements took place at the San Pietro Capofiume meteorological station in northern Italy (44° 39‘N, 11° 37‘E, 11 m a.s.l) during 7 June – 9 July 2012. The measurements were part of the PEGASOS (Pan-European Gas–Aerosol–Climate Interaction Study) Zeppelin campaign where San Pietro Capofiume was one of the ground stations. The meteorological station is located about 30 km northeast from the city of Bologna in the Po Valley (Fig. 1). The Po Valley region is situated between the Alps in the north and the Apennines Mountains in the south-southwest. The mountains surround the valley on three sides and strongly modify both the local and regional air flow patterns in the area (Sogacheva et al., 2007). High levels of anthropogenic

pollutants have been observed in the region due to the emissions from power plants and industrial areas. In addition, the emissions from ship traffic in the Adriatic Sea (Hamed et al., 2007) and long-range transport from Central and Eastern Europe are possible sources of pollutants in the region (Sogacheva et al., 2007).

During the measurement campaign, the total particle concentrations were measured with an Airmodus Particle Size Magnifier (PSM A09; Vanhanen et al., 2011). PSM is a dual-stage mixing-type condensation particle counter. In the first stage, diethylene-glycol is used to activate and grow the particles to about 90 nm in diameter, after which the further growth and the counting of particles is done with a conventional CPC. The cut-off size of the PSM can be changed by altering the mixing ratio of the sample and saturator flow. In this study, the cut-off sizes of 1.5 nm and 1.8 nm were used, and thus, the total concentration of clusters in the size range of 1.5–1.8 nm was obtained. 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.

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). By subtracting the concentration measured with the highest cut-off size of the PSM from the total particle concentration measured with the DMPS, we obtained the total concentration of clusters and particles in the size range of 1.8–3 nm. Furthermore, the number size distributions of positive and negative ions between 0.8 and 42 nm and the number size distributions of all particles between 2 and 42 nm were measured with a Neutral Cluster and Air Ion Spectrometer (NAIS; Kulmala et al., 2012; Mirme and Mirme, 2013). By interpolating the NAIS data, the ion concentrations in the 1.5–1.8 nm and 1.8–3.0 nm size ranges were obtained. However, the NAIS was not working properly in ion mode during 11–21 June, and therefore this period was excluded from the analysis.

In addition to particle size distribution data, meteorological data, including temperature, relative humidity and global radiation, measured at the station were used in the analysis. The data obtained with a SO_2 monitor (model 43i-TLE, Thermo Scientific) were also utilized.

Furthermore, the measurement station was equipped with a ceilometer (Jenoptik CHM15K), which allowed us to monitor the evolution of planetary boundary layer (PBL; Di Giuseppe et al., 2012; Angelini and Gobbi, 2014).

2.2 Determining the concentration of neutral clusters

To study the importance of ion-mediated processes for cluster formation, we calculated the number of neutral clusters originating from the collisions between oppositely charged ions, i.e. recombination products, in the size bins of 1.5–1.8 nm and 1.8–3 nm. The concentration of recombination products in size bin *i* was obtained from (Kontkanen et al., 2013):

$$N_{rec,i} = \frac{\lambda_i \alpha \sum_{j,k} r_{ijk} N_j^+ N_k^-}{CoagS_i}. \quad (1)$$

Here λ_i represents the fraction of stable recombination products that do not break up instantly after their formation in size bin *i*. α is the ion–ion recombination coefficient for which we used the value of 1.6×10^{-6} cm^3 s^{-1} (Hoppel and Frick, 1986; Tammet and Kulmala, 2005). N_j^+ and N_k^- refer to the concentrations of positive and negative ions in size ranges *j* and *k*, respectively, and r_{ijk} tells how large fraction of the recombination products formed in their collisions end up in size bin *i*. CoagS$_i$ is the average coagulation sink for size range *i*. Thus, Eq. (1) takes into account the production of neutral clusters in the collisions between two oppositely charged ions (the term in the numerator) and their loss by coagulation (the term in the denominator). The effect of the condensational growth of clusters was neglected, as has been done in most of the earlier studies discussing the concentrations of recombination products (e.g. Lehtipalo et al., 2009; Kulmala et al., 2013). The production rate of neutral clusters due to ion-ion recombination was calculated from the ion size distribution measured with the NAIS. For the detailed description of the procedure, see Kontkanen et al. (2013). The fraction of stable recombination products, λ_i, was assumed to equal unity. The coagulation loss of clusters because of their collisions onto larger aerosol particles was calculated from DMPS data (Kulmala et al., 2001).

After calculating the concentration of recombination products, we calculated the concentration of neutral clusters ($N_{n,i}$), not originating from ion-ion recombination (from now on we refer to these as just neutral clusters), in the size bins of 1.5–1.8 nm and 1.8–3 nm by subtracting the

concentrations of ions ($N_{ions,i}$) and recombination products ($N_{rec,i}$) from the total cluster concentration ($N_{tot,i}$):

$$N_{n,i} = N_{tot,i} - N_{ions,i} - N_{rec,i} \quad (2)$$

For calculating the concentration of neutral clusters from Eq. (2) 10-minute averaged data from the NAIS ($N_{ions,i}$), and from the PSM and the DMPS ($N_{tot,i}$) were used.

2.3 New particle formation event analysis

The classification of measurement campaign days into new particle formation (NPF) event days and non-event days was done by visually evaluating ion size distribution data from the NAIS (Dal Maso et al., 2005; Hirsikko et al., 2007). The days when new particle formation and growth were observed were classified as NPF event days, while the days with no implication of NPF were assigned as non-event days.

The growth rates of 1.5–3 nm, 3–7 nm and 7–20 nm particles were determined for the identified NPF events. For calculating the growth rates, we used positive ion size distribution data measured with the NAIS and applied the method by Hirsikko et al. (2005). In this method a Gaussian distribution is fitted to the concentration time series at a certain size to determine the moment of maximum concentration. Then, the growth rate is obtained as the slope of a linear least square fit to the moments of maximum concentrations and the corresponding geometric mean diameters of the particles. For the comparison of particle growth rates determined using different instruments and methods, see Yli-Juuti et al. (2011).

The total particle formation rates and ion formation rates at 1.6 nm ($J_{1.6}$) and at 2 nm (J_2) were calculated following the method in Kulmala et al. (2012). When calculating the total particle formation rate, we determined the time derivative of particle concentration and took into account the effects of coagulation loss and the growth out of the studied size range. The accuracy of this method is evaluated in Korhonen et al. (2011). When determining the ion formation rate, the loss of ions by ion-ion recombination and the charging of neutral particles were also included in the calculation. The total particle formation rate at 1.6 nm was determined from the PSM data, while for calculating the total particle formation rate at 2 nm we used NAIS particle size distribution data. The ion formation rates were calculated from the NAIS ion size distributions. For the growth rates needed for the calculations, we used the growth rates determined for 1.5–3 nm size range from the NAIS data. 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).

2.4 Sulfuric acid proxy

To study the connection between the concentrations of sub-3nm clusters and sulfuric acid, we calculated the sulfuric acid concentration from a non-linear statistical proxy derived by Mikkonen et al. (2011):

$$\mathrm{SA_{proxy}} = 8.21 \times 10^{-3} \times k \times \mathrm{Rad} \times [\mathrm{SO_2}]^{0.62} \times (\mathrm{CS} \times \mathrm{RH})^{-0.13} \quad (3)$$

Here k describes the reaction rate coefficient, which depends on air temperature and atmospheric pressure. Rad refers to global radiation, $[SO_2]$ to the concentration of sulfur dioxide and RH to relative humidity. 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). The proxy was calculated only for times when global radiation exceeded 10 W m^{-2}. Mikkonen et al. (2011) concluded that their proxy is suitable for estimating sulfuric acid concentration in a wide range of environmental conditions. Still, as there were no measurements of sulfuric acid concentration during our measurement campaign, the accuracy of the proxy in these specific conditions could not be assessed.

2.5 Trajectory analysis

To investigate the origin of air masses during the measurement campaign, we calculated 24-hour backward trajectories using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (Draxler and Rolph, 2015). Global FNL (Final) meteorological archive generated by the NCEP GDAS (National Centers for Environmental Prediction Global Data Assimilation System) were used in the calculations. For each day we studied trajectories arriving at the measurement site hourly between 10 a.m. and 2 p.m. local winter time (UTC + 1 h) with the arrival height of 100 m. We determined the arrival direction of the air mass by dividing the trajectories into 22.5° sectors. If a trajectory spent over 70% of the last 24 h before arriving to San Pietro Capofiume in a certain sector, that sector was selected to correspond to the arrival direction of the air mass.

3 Results and discussion

3.1 Meteorological conditions in San Pietro Capofiume during the PEGASOS campaign

The weather conditions during the campaign were initially characterized by moderate instability (from 8th to 14th June), which was followed by a series of sunny, hot days with relative humidity (RH) decreasing from day to day. The mean temperature for the campaign (25.5°C) was 3.5°C higher compared to a 15-year climatology for the site (data from the Regional Agency for Environmental Protection, ARPA, of Emilia-Romagna). The average RH was 16% lower than typically, and the cumulated rain (24 mm) was half of the expected amount. In summary, the ambient conditions during the experiment were more representative for a heat-wave period than for an average summer in the Po Valley.

The meteorological conditions prevailing during the campaign resulted in the strong diurnal variation of radiation, temperature and RH. The diurnal cycles of these variables are presented in Fig. 2 for new particle formation (NPF) event days (86% of the days, see Sect. 3.3) and the only non-event day (6 July 2012) in local winter time (UTC + 1 h). For NPF event days the median diurnal cycle and the 25% to 75% percentile range are shown. On NPF event days global radiation started typically increase around 4 a.m. in the morning, and reached its maximum (median value 940 W/m^2) at noon (Fig. 2a). Temperature began to increase from its night-time values (about 20 °C) at the same time with the radiation and was highest (about 33 °C) around 3 p.m. (Fig. 2b). The diurnal cycle of RH was opposite to that of temperature: RH was highest (about 84 %) early in the morning and lowest (about 30%) in the afternoon (Fig. 2b). On the non-event day global radiation increased in the morning slightly slower than typically on event days, and after reaching its maximum (820 W/m^2) around noon the radiation level dropped rapidly. Correspondingly, temperature also decreased in the afternoon being at that time 6–8 °C lower than typically on NPF event days. On the other hand, in the morning of the non-event day temperature was similar, or even slightly higher, than typically on event days. Furthermore, starting from 6 a.m. RH was higher on the non-event day than on event days, exceeding 60% in the afternoon. The results support previous studies from San Pietro Capofiume where NPF events have been observed to occur on days with high solar radiation and low RH (Hamed et al., 2007; Sogacheva et al., 2007).

Figure 2a also presents the diurnal variation of PBL height. On NPF event days the progressive increase of the mixing layer from about 250 m to 1 700 m can be observed between 7 a.m. and

3 p.m. Therefore, the first steps of the photochemical processes observed at the station were triggered by reactions occurring in a rather thin atmospheric surface layer. Conversely, in the late morning and in the afternoon hours, the thickness of the PBL was great enough to allow the entrainment of air masses with their burden of chemical compounds travelling over long distances. On the non-event day the PBL height increased higher than typically on event days reaching about 2000 m. However, similarly as radiation, the PBL height quickly decreased in the afternoon being at that time about 1000 m lower than the PBL height typically on event days. Further analysis of ceilometer data reveals that low-level clouds were present in the morning and rainfall occurred between 2 p.m. and 3 p.m. on the non-event day, which explains the observed behavior of radiation, RH and the PBL height.

The effect of PBL height on background aerosol concentrations can be seen in the median diurnal variation of condensation sink (Fig. 2c). Condensation sink was highest around 2 a.m. when boundary layer was still thin. The maximum value of condensation sink was higher on the non-event day (0.023 s^{-1}) than typically on NPF event days (median value 0.015 s^{-1}). During the early morning, when the PBL started to form, condensation sink rapidly decreased and around 9 a.m. reached its daytime level (about 0.01 s^{-1} both on NPF event days and on the non-event day). During the day, when mixing layer extended higher in the atmosphere, condensation sink stayed low starting to increase again after 6 p.m. Our observation on the lower condensation sink in the mornings of NPF event days compared to the non-event day is consistent with Hamed et al. (2007), who showed that low condensation sink favor particle formation in San Pietro Capofiume.

The diurnal patterns of SO_2 concentration and sulfuric acid proxy were also slightly different on NPF event days and on the non-event day (Fig 2d). On event days SO_2 concentration started to rise from its low night-time values (median value 0.13 ppb) around 5 a.m. reaching its maximum (about 0.9 ppb) around 9 a.m. After that SO_2 concentration decreased until having a second peak (about 0.8 ppb) around 20 p.m. The low concentration of SO_2 at night is likely due to its deposition on the ground in the nocturnal boundary layer, while the increase in the morning is induced by the mixing of the boundary layer allowing the entrainment of SO_2 from aloft. On the non-event day, SO_2 concentration was throughout the day clearly lower than typically on event days. The increase in the concentration occurred later than on event days (around 10 a.m.), and the concentration reached only about 0.6 ppb. The second peak in the evening was also clearly lower (about 0.3 ppb) than on event days. The diurnal cycle of sulfuric

acid proxy on NPF event days resembles the diurnal cycle of radiation; the concentration starts to increase around 4 a.m. in the morning and is highest (median value 2.3×10^7 cm^{-3}) around noon. On the non-event day, sulfuric acid proxy stays lower than on event days, its maximum value being about 1.7×10^7 cm^{-3}. In addition, the value of the proxy starts to increase later than on event days, reflecting the late increase in SO_2 concentration. These results are in agreement with Hamed et al. (2006), who observed that in San Pietro Capofiume daytime SO_2 concentrations are clearly higher on NPF event days than on non-event days.

3.2 Concentrations of sub-3nm clusters

A high number of sub-3nm clusters was observed in San Pietro Capofiume during the measurement period (Fig. 3). The total concentration of 1.5–1.8 nm clusters varied from 610 to 11 930 cm^{-3} (5% and 95% percentile) with the median concentration of 2140 cm^{-3}. The total concentration of 1.8–3.0 nm clusters varied from 2300 to 30 150 cm^{-3} (5% and 95% percentile), while the median concentration was 7980 cm^{-3}. The majority of the observed sub-3nm clusters were electrically neutral. The median concentrations of neutral clusters were 2090 cm^{-3} and 7950 cm^{-3} in the size bins of 1.5–1.8 nm and 1.8–3 nm, respectively. The median positive ion concentrations were 20 cm^{-3} and 4 cm^{-3} in the same size bins, and the median negative ion concentration was 6 cm^{-3} in both of the size bins. The concentrations of recombination products were also low: the median concentrations were 11 cm^{-3} and 5 cm^{-3} in the size bins of 1.5–1.8 nm and 1.8–3 nm. 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. On the other hand, the lower negative ion concentration can also be partly related to the electrode effect, causing the accumulation of positive ions close to the Earth's surface (Hoppel et al., 1967).

Our results are in agreement with the earlier measurements from boreal forest in Finland, where a continuous population of sub-3nm neutral clusters has been observed (Lehtipalo et al., 2009; Kulmala et al., 2013). However, the clusters concentrations observed in San Pietro Capofiume are about five times higher than the concentrations in the same size range in boreal forest. The observed cluster concentrations also exceed the concentrations of sub-3nm clusters reported from a high-altitude site in France (Rose et al., 2015) and from two urban sites in the United States (Yu et al., 2014). On the other hand, at polluted sites in China, the sub-3nm cluster concentrations were observed to be of the same order of magnitude as in San Pietro Capofiume

(Xiao et al., 2015; Yu et al., 2015). This indicates that the formation of sub-3nm clusters may be favored in areas where anthropogenic emissions of precursor vapors are high. Furthermore, our results support the earlier observations from boreal forest, where the contribution of ion-ion recombination to atmospheric cluster formation has been shown to be minor (Lehtipalo et al., 2009; Kontkanen et al., 2013).

3.3 New particle formation

NPF events were frequently observed during the measurement campaign (see Fig. 4). During the measurement period 86% (19/22) of the days, from which we had NAIS data, were classified as NPF event days, while only one day was classified as a clear non-event case. On average, NPF is detected at the site less frequently, on 40–45 % of the days in June and on 65–70% of days in July (Hamed et al., 2007; Manninen et al., 2010). High frequency of NPF events during our measurement campaign was likely related to favorable meteorological conditions with high solar radiation and low RH (see Sect. 3.1). Figure 5 shows the evolution of ion size distribution on a typical NPF event day (28 June) during the measurement campaign. The onset of NPF event can be observed around 7 a.m. and the growth of the ions can be followed until 5 p.m. in the evening.

The statistics of particle growth rates for the NPF events are shown in Table 1. The median growth rates in the size ranges of 1.5–3 nm, 3–7 nm and 7–20 nm were 4.3 nm h^{-1}, 6.0 nm h^{-1} and 7.2 nm h^{-1}. Thus, the growth rate generally increased with the increasing particle size, which has been observed also at other measurement sites (Yli-Juuti et al., 2011; Kuang et al., 2012; Kulmala et al., 2013), and predicted by the so-called nano-Köhler theory describing the activation of nanometer-sized clusters by organic vapors (Kulmala et al., 2004b). By using BSMA (Balanced Scanning Mobility Analyzer) measurements, Manninen et al. (2010) obtained the median growth rate of 1.5 nm h^{-1} for 1.5–3 nm particles in San Pietro Capofiume. 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 summertime.

Table 2 presents the statistics of particle formation rates at 1.6 nm and at 2 nm during NPF events. The median formation rate of 1.6 nm clusters, 45 cm^{-3} s^{-1}, was one order of magnitude higher than the median formation rate of 2 nm clusters, 6.8 cm^{-3} s^{-1}. In earlier field

measurements in boreal forest, Finland, the median particle formation rates were 5.9 cm^{-3} s^{-1} at 1.5 nm and 1.9 cm^{-3} s^{-1} at 2 nm (Kulmala et al., 2013). On the other hand, at a polluted site in Shanghai, China, the average formation rate of 1.3 nm clusters was observed to be 188 cm^{-3} s^{-1} (Xiao et al., 2015). Thus, it seems that the formation rates of sub-3nm clusters are in San Pietro Capofiume higher than in clean boreal forest environment but still lower than at a polluted urban site. This indicates that high background aerosol concentrations do not necessarily inhibit the formation of sub-3nm clusters if the concentrations of precursor vapors are high enough. The median condensation sink in San Pietro Capofiume was 1.1×10^{-2} s^{-1} during the measurement period. In boreal forest, Finland, typical condensation sink on NPF event days has been observed to be about 2×10^{-3} s^{-1} (Dal Maso et al., 2005; Kulmala et al., 2013), and in Shanghai, China, 6×10^{-2} s^{-1} (Xiao et al., 2015).

The median formation rates of 1.6 nm positive and negative ions (0.19 cm^{-3} s^{-1} and 0.06 cm^{-3} s^{-1}) were two orders of magnitude lower than the formation rate of 1.6 nm total clusters (Table 2). In addition, the median formation rates of 2 nm positive ions (0.12 cm^{-3} s^{-1}) and negative ions (0.08 cm^{-3} s^{-1}) were one order of magnitude lower than the formation rate of 2 nm total clusters. Thus, neutral pathways seem to dominate particle formation in San Pietro Capofiume. These results are consistent with the earlier observations from boreal forest in Finland and at a high-altitude site in France, where the formation rate of 1.5 nm total clusters has been found to clearly exceed the formation rate of 1.5 nm ions (Kulmala et al., 2013; Rose et al., 2015). Manninen et al. (2010) reported slightly lower values for the median formation rates of 2 nm ions (0.06 cm^{-3} s^{-1} for both polarities) based on their BSMA measurements in San Pietro Capofiume. 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.

To further investigate the contribution of ions to particle formation, we calculated the ion-induced nucleation fraction for each NPF event by dividing the ion formation rate by the total formation rate. The median ion-induced nucleation fraction was 0.7% at 1.6 nm and 3.0% at 2 nm. 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. This further demonstrates that ions have only a minor contribution to the formation of sub-3nm clusters in San Pietro Capofiume. The higher ion-induced nucleation fraction at 2 nm than at 1.6 nm suggests that ions at 2 nm may be formed by coagulation between small ions and neutral

clusters. In previous studies the ion-induced nucleation fraction has been observed to be typically low, less than 10%, in the continental boundary layer (Iida et al., 2006; Manninen et al., 2010).

3.4 Diurnal variation of cluster concentrations and formation rates

Figure 6 shows the median diurnal variation of the concentrations of neutral clusters, charged clusters and recombination products on NPF event days and on the only non-event day. In addition, the variation of PBL height is presented. The concentrations of neutral 1.5–1.8 nm and 1.8–3.0 nm clusters were high throughout the day on NPF event days and on the non-event day. On NPF event days the neutral cluster concentrations had maxima around 9 a.m., which could not be observed on the non-event day. 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. The daytime maximum on NPF event days can also be detected in the concentrations of ions and recombination product in the size bin of 1.8–3.0 nm. Nevertheless, the peak ion concentrations were about three orders of magnitude lower than those of neutral clusters. In the smaller size bin (1.5–1.8 nm) these maxima were not as clear. The reason for this is that small ions are continuously formed in the atmosphere as a result of ionization of air molecules, while larger ions are usually present only during NPF events (e.g. Hirsikko et al., 2011). The observed diurnal cycle of the cluster concentrations is generally similar as in the earlier observations made in boreal forest, Finland (Kulmala et al., 2013), and at urban sites in the United States and China (Yu et al., 2014; Xiao et al., 2015; Yu et al., 2015).

To study the contribution of ions to cluster concentrations, we also examined the median diurnal variation of the fraction of ions of all clusters on NPF event days (Fig. 7). The ion fraction in the size bin of 1.5–1.8 nm varied between 0.3% and 2%. The lowest values were obtained slightly after 9 a.m., which is due to the strong increase in the neutral cluster concentration during NPF event (Fig. 6). In the size bin of 1.8–3 nm, the ion fraction was most of the time very low (about 0.2%), but peaked before 9 a.m. reaching 0.5%. 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 charged clusters to activate earlier than neutral clusters when the concentration of low-volatile vapors increases in the morning. This may indicate that ion-mediated nucleation pathways could be more significant in the conditions with low precursors vapor concentrations.

In Fig. 8 the median diurnal variations of particle formation rates are presented together with the PBL height for NPF event days and for the only non-event day. The formation rate of 1.6 nm total clusters varied between 8 and 68 cm^{-3} s^{-1} on NPF event days, reaching the highest values around 9 a.m. On the non-event day the formation rate was lower, varying between 2 and 14 cm^{-3} s^{-1}. Similarly, the formation rate of 2 nm clusters had a maximum of 7 cm^{-3} s^{-1} on NPF event days, and on the non-event day it varied between 0.1 and 3 cm^{-3} s^{-1}. The formation rates of ions were at both sizes clearly lower than the total formation rates. The maximum formation rate of 1.6 nm ions on NPF event days was 0.19 cm^{-3} s^{-1} for positive ions and 0.09 cm^{-3} s^{-1} for negative ions. At 2 nm, the corresponding maximum formation rate was 0.13 cm^{-3} s^{-1} for positive ions and 0.11 cm^{-3} s^{-1} for negative ions. On the non-event day the ion formation rates were even lower than on event days. Overall, these results suggest that sub-3nm clusters are formed continuously, also outside NPF events. Furthermore, as concluded already above, neutral nucleation mechanisms seem to dominate in San Pietro Capofiume. Our results support earlier observations obtained in field measurement in boreal forest by Kulmala et al. (2013).

When comparing the diurnal variations of cluster concentrations and their formation rates with the diurnal cycle of PBL height and other meteorological parameters, similarities can be found. At the same time as the concentrations and formation rates of clusters started to increase in the morning of NPF event days, after 7 a.m., the PBL height also started to increase. Furthermore, at this time radiation, temperature and SO_2 concentration had already started to rise from their low nigh-times values and, reversely, RH and condensation sink were decreasing (Fig. 2). This indicates that the sunrise can be important for the formation of atmospheric clusters due to several processes. Firstly, the build-up of PBL, induced by the heating of solar radiation, dilutes the background aerosol concentration and thus reduces the condensation sink. Furthermore, the mixing of the boundary layer increases the concentration of SO_2, which is oxidized to sulfuric acid. Solar radiation also triggers the photochemical production of other low-volatile precursor vapors, which could participate in the formation of clusters. Finally, increasing temperature also lowers RH. On the other hand, it needs to be noted that the formation of sub-2nm clusters was observed to take place continuously, also at night (see Fig. 8). 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).

3.5 Effect of sulfuric acid concentration and condensation sink on cluster concentrations

San Pietro Capofiume is located in the industrialized Po Valley with many emission sources for anthropogenic pollutants. According to Sogacheva et al. (2007), more than 40% of SO_2 emissions over the Po Valley can be observed at the San Pietro Capofiume station. SO_2 is a precursor for sulfuric acid that is known to be a key compound in atmospheric cluster formation (e.g. Weber et al., 1997; Sipilä et al., 2010; Kirkby et al., 2011). To investigate the importance of sulfuric acid for cluster formation in San Pietro Capofiume, we studied the correlation between the concentrations of neutral and charged clusters and sulfuric acid proxy. Furthermore, to see how the concentrations of large background aerosol particles affect cluster concentrations, the correlation between cluster concentrations and condensation sink was examined.

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. 9). For both neutral and charged clusters the positive correlation was stronger in the size bin of 1.8–3 nm (R = 0.64 for neutral clusters and R = 0.67 for ions) than in the size bin of 1.5–1.8 nm (R = 0.52 for neutral clusters and R = 0.51 for ions). This is in accordance with Kulmala et al. (2013), who observed that the smallest, sub-1.7 nm, clusters correlated with sulfuric acid less strongly than larger clusters.

The relation between the sub-3nm cluster concentrations and condensation sink is presented in Fig. 10. It seems that the concentration of neutral clusters does not have a negative correlation with condensation sink as one would expect. This indicates that in San Pietro Capofiume the formation of neutral clusters may, at least partly, be linked to anthropogenic emissions with high concentrations of low-volatile precursor vapors but also high condensation sink. Furthermore, ions had a negative correlation with the condensation sink especially in the size bin of 1.5–1.8 nm (R = -0.56). In the size bin of 1.8–3 nm the negative correlation was weaker (R = -0.33). We also investigated the correlation between the cluster concentrations and the ratio of 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).

3.6 Effect of air mass origin

By using back-trajectory analysis, we investigated how the air mass origin affects the sub-3nm cluster concentrations, and their precursors and sinks in San Pietro Capofiume. Figure 11 illustrates the air mass arrival directions and their relation to the total concentration of 1.8–3.0 nm clusters, sulfuric acid proxy, and condensation sink in San Pietro Capofiume around midday (between 10 a.m. and 2 p.m.). A clear majority of air masses arrived to San Pietro Capofiume from northeastern to eastern directions and from the southwest during the measurement campaign. When air masses were coming from northeastern to eastern directions the sub-3nm cluster concentrations were most of the time high ($>3\times10^4$ cm^{-3}). When air masses originated from the southwest, lower concentrations were more frequent. Moreover, the southwestern direction was often related to high condensation sink ($>1.2\times10^{-2}$ s^{-1}). On the other hand, high values of condensation sink were observed also when air masses were coming from the northeast. For sulfuric acid proxy, there was no clear difference between the northeastern and southwestern directions, but high concentrations ($>2.4\times10^7$ cm^{-3}) were linked to both of these directions.

All in all, it seems that the northeastern direction was more favorable for the formation of sub-3nm clusters than the southwestern direction during our measurement campaign. In previous studies air masses related to particle formation have also been observed to arrive to San Pietro Capofiume mostly from eastern directions (Hamed et al., 2007; Sogacheva et al., 2007). Furthermore, Hamed et al. (2007) reported that in all seasons except summer, the eastern directions were associated with the lower value of condensation sink than the western directions. In summer, they did not observe a clear difference in condensation sink between eastern and western air masses. This is in agreement with our results which do not show significantly lower condensation sink related to the northwestern direction than the southwestern direction. Thus, it seems that during our measurement campaign the precursor vapors of the clusters and large background aerosol particles, which act as a sink for clusters, may have originated from the same sources. This is consistent with the fact that no negative

correlation was found between neutral sub-3nm clusters and condensation sink, as discussed in Sect. 3.5. The possible sources of background aerosol particles and precursor vapors include anthropogenic emissions from power plants and industrial areas in the Po Valley, ship traffic in the Adriatic Sea, and long-range transport from Central and Eastern Europe (see Fig. 1) (Hamed et al., 2007; Sogacheva et al., 2007).

4 Conclusions

A high concentration of sub-3nm clusters was observed in San Pietro Capofiume measurement site during the PEGASOS campaign (7 June – 9 July 2012). The majority of clusters were electrically neutral. The observed sub-3nm cluster concentrations were of the same order of magnitude as at polluted sites in China (Xiao et al. 2015; Yu et al., 2015), and higher than in clean boreal forest in Finland (Kulmala et al., 2013) and at urban sites in the United States (Yu et al., 2014).

New particle formation (NPF) events were observed during the measurement period very frequently, on 86% of the days. The particle formation rates during events were higher than in clean boreal forest environment but lower than at a highly polluted urban site (Kulmala et al., 2013; Xiao et al., 2015). Furthermore, the median formation rates of ions were clearly lower than the formation rates of total clusters at all sizes. This indicates that neutral pathways dominate the sub-3nm cluster formation in San Pietro Capofiume, similarly as in boreal forest (Kulmala et al., 2013). The median condensation sink during the measurement period was relatively high, which demonstrates that high background aerosol concentrations do not necessarily inhibit the formation of sub-3nm clusters.

The neutral cluster concentrations were found to have maxima in the mornings of NPF event days, which were absent on the non-event day. Still, the formation of the smallest clusters was observed to take place continuously, also outside NPF events. The increase in the cluster concentration in the morning took place simultaneously with the build-up of planetary boundary layer (PBL). In addition, radiation, temperature and SO_2 concentration were rising and condensation sink and RH declining at that time. Thus, the changes in the local meteorological conditions triggered by the sunrise in the morning may be important drivers of cluster formation at the San Pietro Capofiume station.

The sub-3nm cluster concentrations were observed to have a positive correlation with sulfuric acid proxy. This suggests that sulfuric acid may have an important role in the formation of sub-

3nm clusters in San Pietro Capofiume, as has also been observed at other measurement sites (Kulmala et al., 2013; Yu et al., 2014). On the other hand, it is likely that other compounds, e.g. low-volatile organic vapors, also participate in the formation of clusters. The concentration of charged clusters was found to have a negative correlation with condensation sink, while no relation between the neutral cluster concentrations and condensation sink was observed. This result, together with the back-trajectory analysis, indicates that the precursor vapors of clusters and background aerosol particles, acting as their sink, may have originated from the same sources. The potential sources include anthropogenic emissions from power plants and industrial areas in the Po Valley, maritime traffic in the Adriatic Sea, and long-range transport from Central and Eastern Europe (Hamed et al., 2007; Sogacheva et al., 2007).

Acknowledgements

This research was supported by the European Commission under the Framework Programme 7 (PEGASOS project, FP7-ENV-2010-265148), the European Research Council (ERC) Advanced Grant (ATM-NUCLE, 227463), and the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 656994. The support by the Academy of Finland Centre of Excellence program (project no. 1118615 and 272041) is also gratefully acknowledged.

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Table 1: Growth rates of particles during NPF events. The median values and the range from 5- to 95-percentile are shown. The growth rates were determined from the positive ion size distributions measured with the NAIS.

Size range	**Growth rate [nm h^{-1}]**
1.5–3.0 nm	4.3 (1.0–10.0)
3.0–7.0 nm	6.0 (2.6–12.9)
7.0–20.0 nm	7.2 (3.8–13.8)

Table 2: The formation rates of all clusters and ions during NPF events. The median values and the range from 5- to 95-percentile are shown. The formation rates of all clusters at 1.6 nm were determined from PSM data. The formation rates of ions at 1.6 nm and all clusters and ions at 2 nm were determined from NAIS data.

Size	Clusters	Formation rate [cm^{-3} s^{-1}]
1.6 nm	All clusters	45 (23–53)
1.6 nm	Positive ions	0.19 (0.09–0.32)
1.6 nm	Negative ions	0.06 (0.03–0.08)
2.0 nm	All clusters	6.8 (2.7–38.5)
2.0 nm	Positive ions	0.12 (0.05–0.25)
2.0 nm	Negative ions	0.08 (0.03–0.19)

Figure 1: The map of Northern Italy, where the location of the San Pietro Capofiume (SPC) measurement site is shown with a red marker. Map data provided by Google.

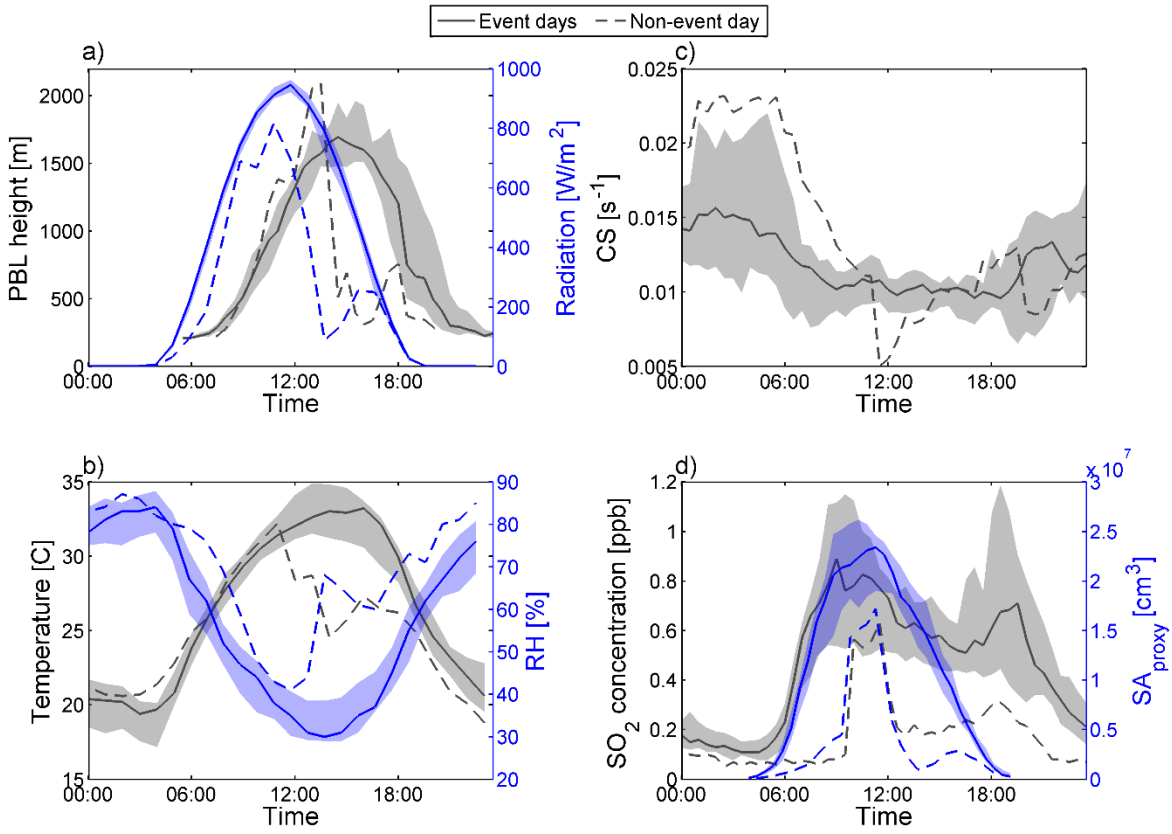


Figure 2: The diurnal variation of different variables during the measurement campaign: a) PBL height (grey) and global radiation (blue), b) temperature (grey) and relative humidity (RH; blue), c) condensation sink (CS), d) SO_2 concentration (grey) and sulfuric acid proxy (SA_{proxy}; blue). The median diurnal pattern on NPF event days is shown as solid lines, and the 25% to 75% percentile range as the shaded area. The diurnal variation on the only non-event day (6 July 2012) is shown as dashed lines. Time is UTC + 1 h.

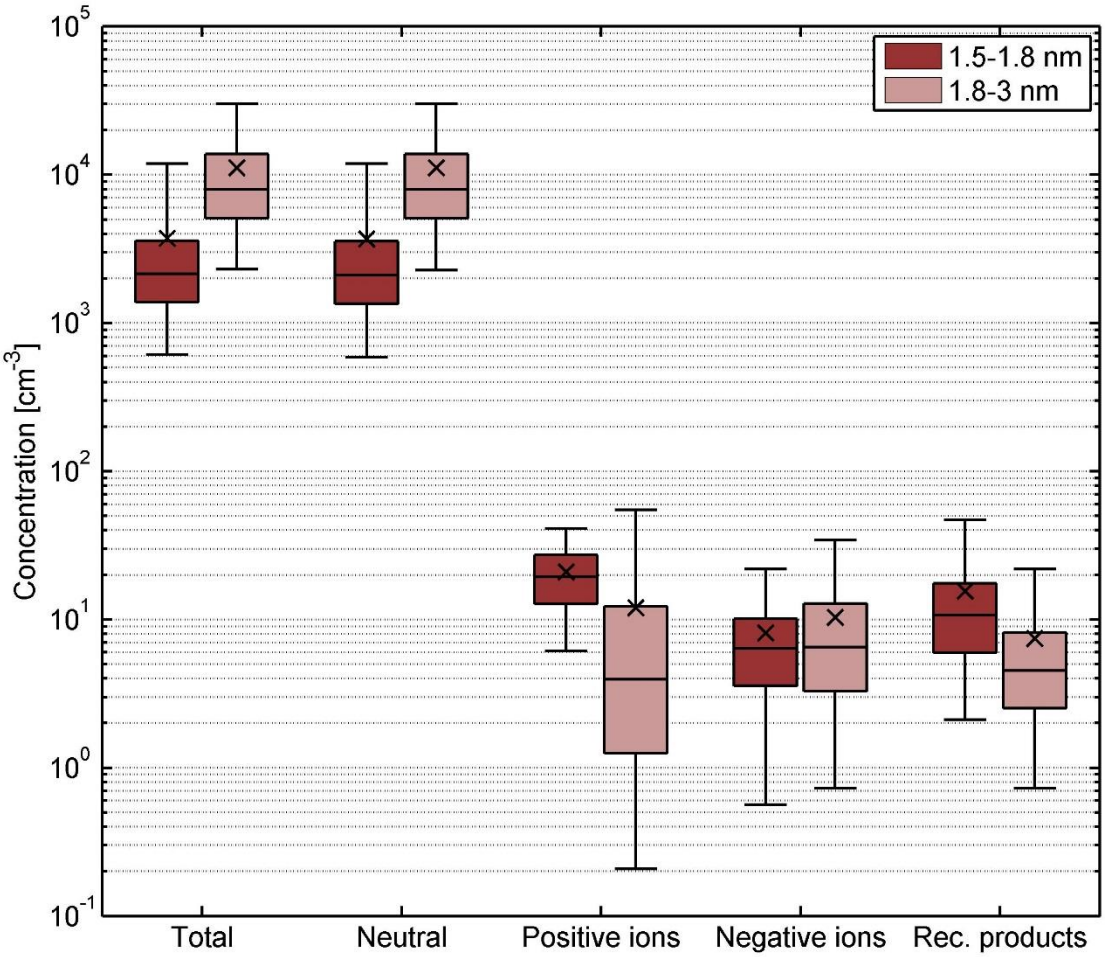
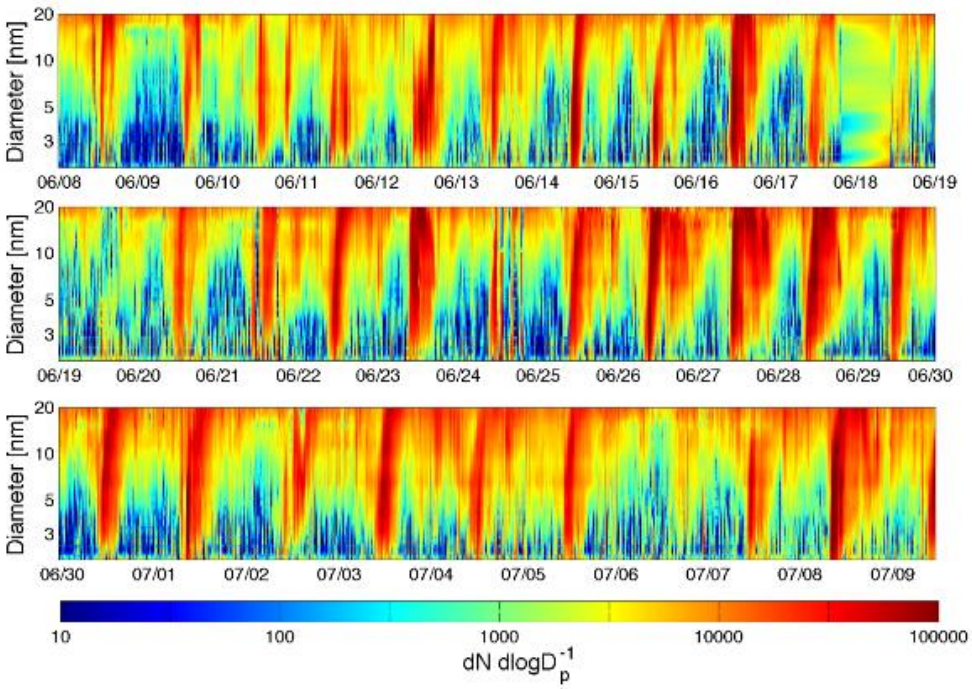


Figure 3: The median concentration of all clusters, neutral clusters, positive ions, negative ions and recombination products in the two size bins (1.5–1.8 nm and 1.8–3.0 nm). The edges of the boxes show the 25- and 75-percentiles and the centers of the boxes represent the median values. The mean values are presented with black crosses. The error bars show the 5- and 95-percentile values.



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2 **Figure 4:** Time series of particle size distribution measured with the NAIS during 8 June – 9
3 July 2012 in San Pietro Capofiume.

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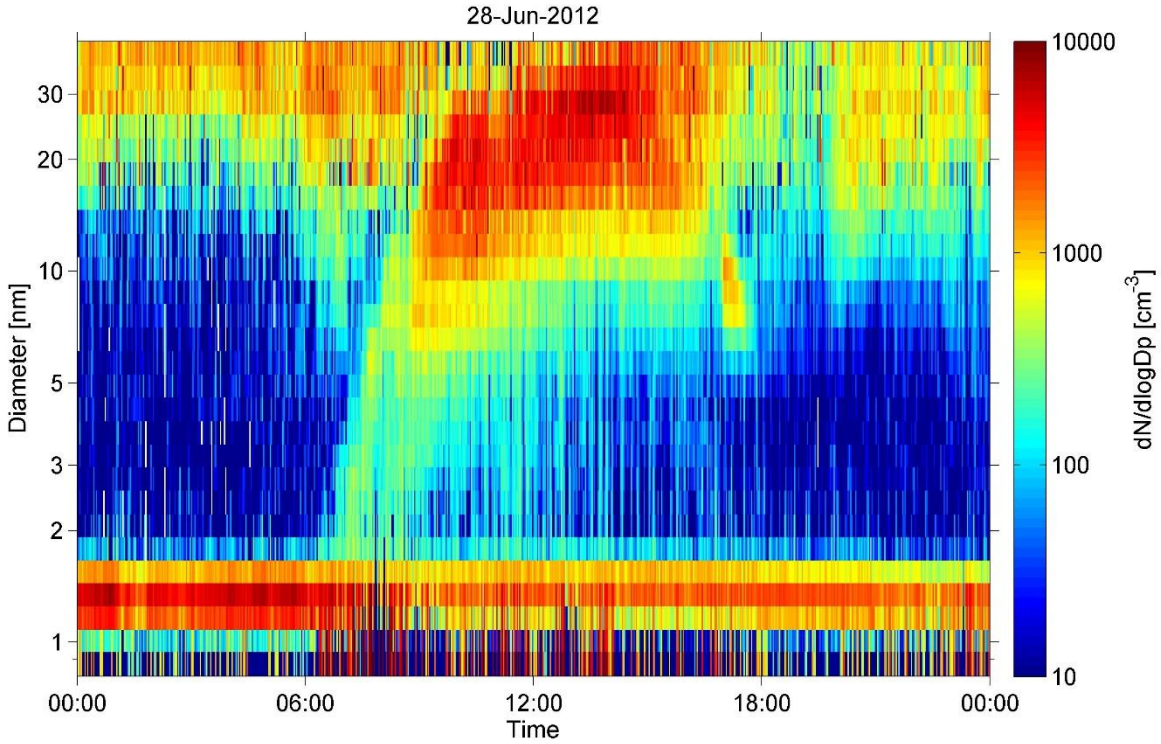


Figure 5: The size distribution of positive ions on a typical new particle formation event at the San Pietro Capofiume station (28 June 2012).

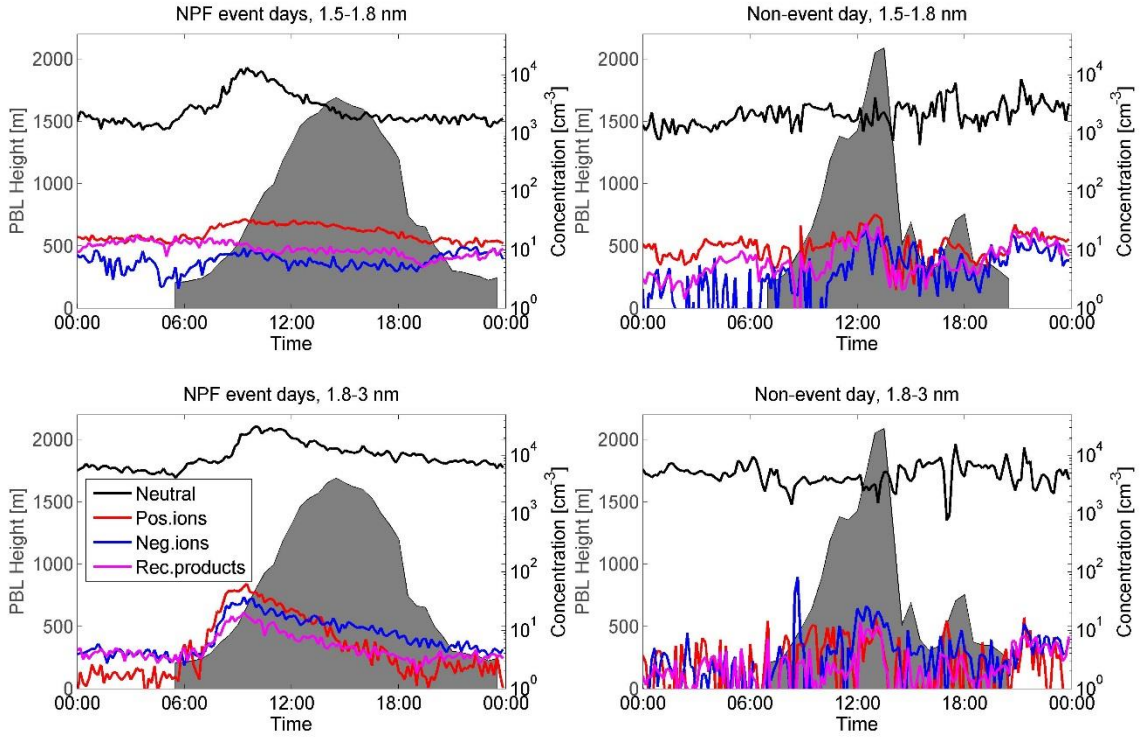


Figure 6: The median diurnal variation of the concentrations of neutral clusters (black line), positive ions (red line), negative ions (blue line) and recombination products (magenta line) on NPF event days and on the only non-event day (6 July 2012). In addition, the PBL height is shown in grey. Time is UTC + 1 h.

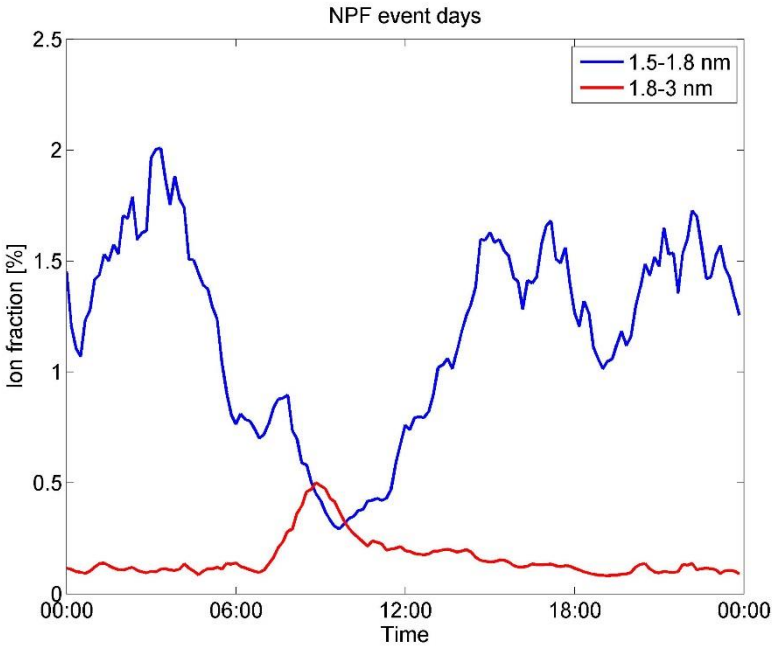


Figure 7: The median diurnal variation of the fraction of ions of all clusters in the size bins of 1.5–1.8 nm (blue line) and 1.8–3.0 nm (red line) on NPF event days. Time is UTC + 1 h.

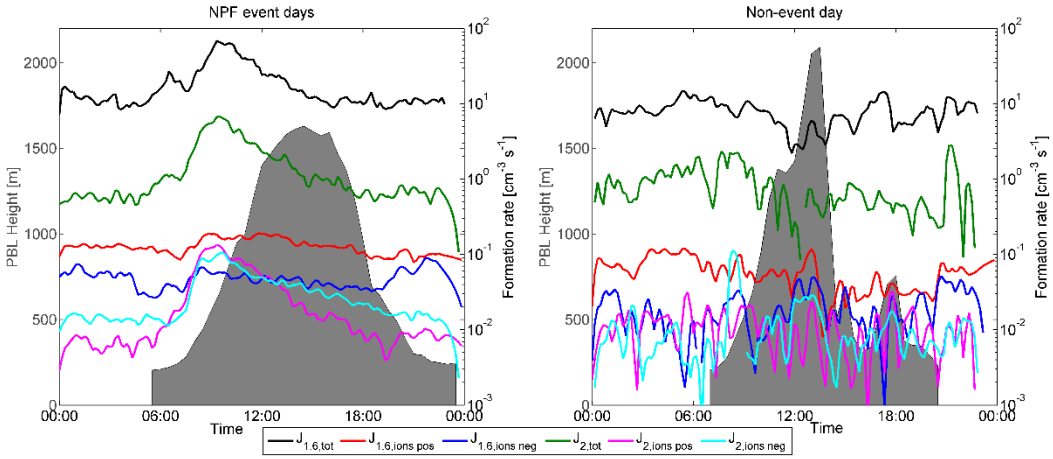


Figure 8: The median diurnal variation of the cluster formation rates at 1.6 nm and 2 nm on NPF event days and on the only non-event day (6 July 2012). The PBL height is shown in grey. In the subscripts numbers refer to the size of the cluster in nanometers and "tot" refers to total clusters, "pos" to positive ions and "neg" to negative ions. Time is UTC + 1 h.

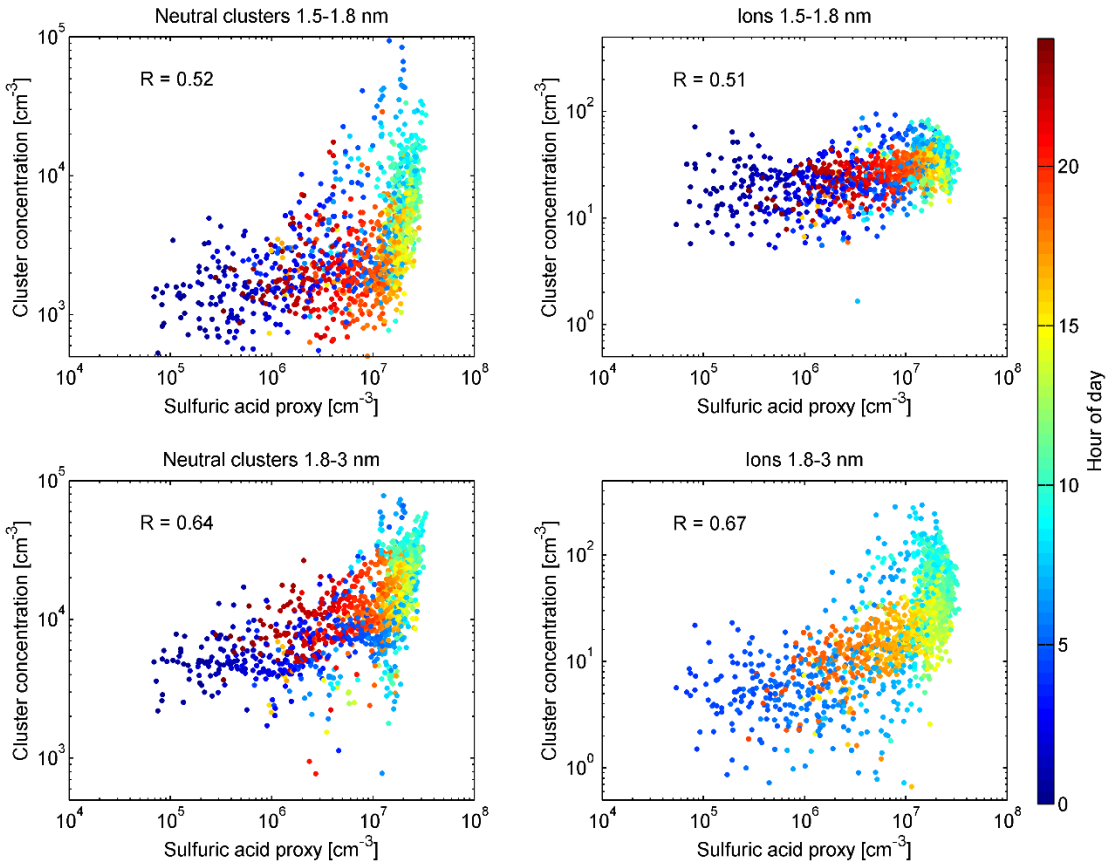


Figure 9: The correlation between the neutral and charged 1.5–1.8 nm and 1.8–3.0 nm clusters and sulfuric acid proxy. The color bar shows the hour of day. The correlation coefficients (R) are presented in the figures.

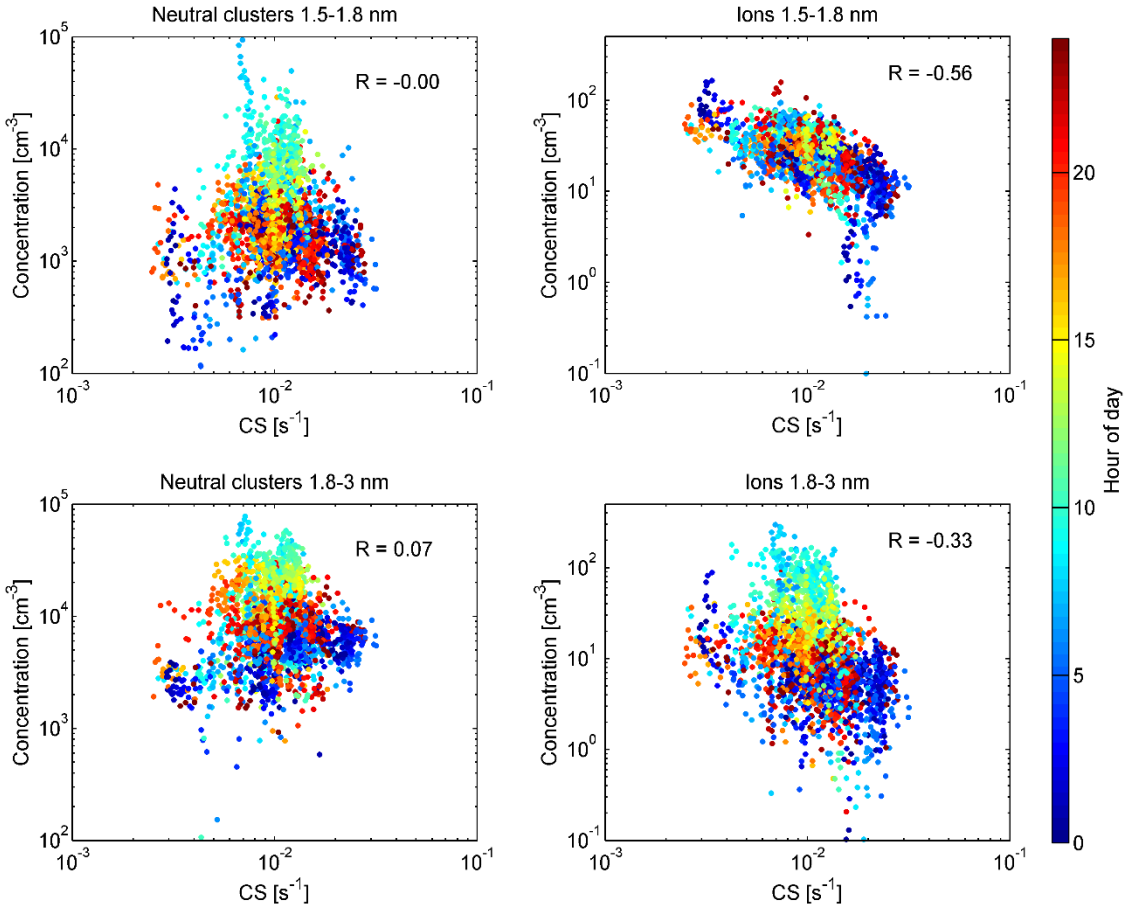
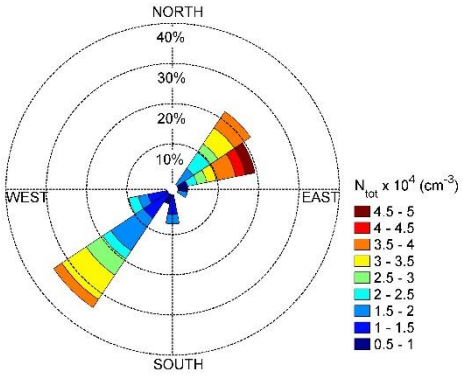


Figure 10: The correlation between the neutral and charged 1.5–1.8 nm and 1.8–3.0 nm clusters and condensation sink (CS). The color bar shows the hour of day. The correlation coefficients (R) are presented in the figures.



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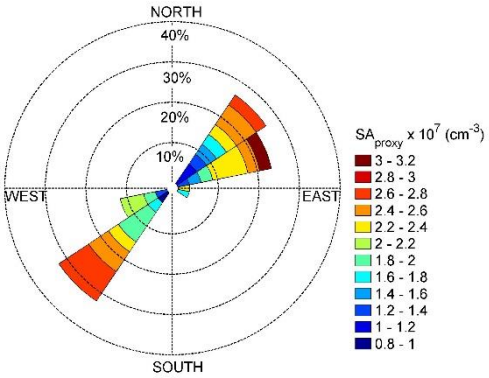

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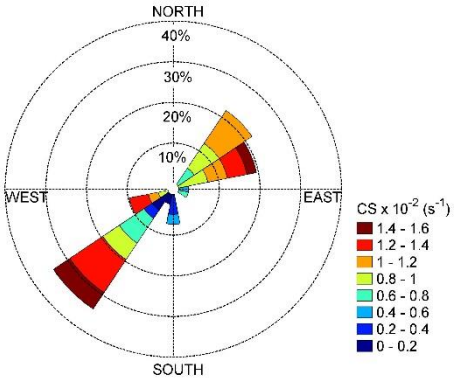

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4 **Figure 11:** Air mass arrival directions and their relation to the total concentration of 1.8–3.0
5 nm clusters (N_{tot}), sulfuric acid proxy (SA_{proxy}) and condensation sink (CS) in San Pietro
6 Capofiume around midday (between 10 a.m. and 2 p.m.). The length of the sectors illustrates
7 how frequently an air mass trajectory arrived from that direction. The color of the sectors shows
8 the value of the measured variable in San Pietro Capofiume at the arrival time of the trajectory.