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

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 back-trajectories.

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.

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.

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).

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?

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 non-event day compared to event days (P33089, l11-12).

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

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).

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…

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?

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).

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.

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?

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