Review of Casquero-Vera et al. "New particle formation at urban and high-altitude remote sites in the south-eastern Iberian Peninsula" by Anonymous Referee #2

We would like to acknowledge the work done by the referee in the revision of our manuscript. We appreciate his/her effort and contributions to improve the quality of the paper. Our responses to the reviewer's comments are detailed below. Our answers to reviewer are shown in bold and the changes inserted in the manuscript are noted here in italic and between quotation marks. The changes in the new version of the manuscript are noted in red.

Response to referee #2:

The MS mainly deals with investigating the aerosol size distributions in the diameter range of 4-500 nm measured simultaneously at two close locations with rather different altitudes in southern Spain during an intensive summer campaign to study the occurrence frequency and other characteristics of NPF events. It is a very complex and extended study. It is of interest for international research community, and I suggest that it is published in the ACP. There are, however, several issues to be improved or corrected.

A point by point response is included below.

1) A general comment. This MS is not easy to read since it contains a large variety of details, which are sometimes not well organized. The authors may want to improve several of its parts (e.g. P15, L26–P16, L14).

Following reviewers' suggestions, we have rewritten the paragraph P16, L10–25 as follows:

"Finally, the chemical composition of desert dust particles (acting as CS) may be another important factor that can play a significant role in the occurrence of NPF events during dust events. In fact, recent laboratory and observational studies (Dupart et al., 2012; Nie et al., 2014) revealed that the presence of TiO_2 and Fe_2O_3 (which are common components of mineral dust) under UV light could promote the occurrence of NPF can enhance the formation of OH and other radicals that favour oxidation reactions, promoting the occurrence of NPF during dusty conditions. These components, acting as catalysts, are not consumed in the photo-catalytic reaction and can accelerate atmospheric photochemistry repeatedly. The PM_{10} elemental analysis shows that both components reached their highest concentrations on 25 and 26 June, with TiO_2 concentrations of 0.24 µg m^{-3} on both days and F_2O_3 concentrations of 1.91 and 1.89 µg m^{-3} on 25 and 26 June, respectively (Table 3). It is worth noting that the effectiveness of photochemical reactions in promoting the occurrence of NPF depends largely on the available precursor gases. Thus, the increased TiO_2 and F_2O_3 concentrations together with the high concentrations of H_2SO_4

and VOCs observed on 26 June, could explain, at least partly, the occurrence of NPF and the observed high formation rates during this dusty day (26 June). However, although the concentrations of TiO_2 and F_2O_3 on June 25 (non-event day) were high and comparable to those observed on 26 June, the low availability of precursor gases on this dusty day seems to be the cause of the non-occurrence of NPF event. Summarizing, these findings suggest that TiO_2 and Fe_2O_3 could promote NPF events during dusty conditions, but the availability of VOCs seems to be the main factors controlling the occurrence of NPF events in this area. To improve our understanding in this topic, further investigation accompanied by multiplatform measurement campaigns is needed."

And in the last paragraph of section 3.2 we made the following change:

"While regional NPF events are usually observed after 11:00 UTC at SNS station probably due to the upslope transport of precursors vapours from lower altitudes, at UGR urban site, we observed the frequent occurrence of a local event (burst event) around 07:00-08:00 UTC followed by another event lasting for few hours (see Fig. S2). First event at urban site coincides with morning traffic rush hours and could be attributed to the so-called delayed primary particles which are formed in the atmosphere from precursor gases released from hot vehicle exhaust after it dilutes and cools in ambient air (Rönkkö et al., 2017). This local event is followed by another event that is associated with the occurrence of regional NPF events at both stations (Fig. 3). The regional NPF events at UGR station appear in the time range from 9:00 UTC to 12:00 UTC, while NPF events at SNS station are usually observed after 11:00 UTC. It is worth to mention that the production of 4 nm particles can be observed at SNS even though their production has already ended at UGR, which suggests that completely new particles are being formed at high altitudes."

2) P12, L3–9 and L26–30: The discussions the roles and importance of H2SO4 and partially of CS in the formation process at the sites seem to be speculative. The authors should provide further firm evidence and additional explanations of their ideas, or they should reduce and simplify this part.

We have reduced both paragraphs as follows:

"In order to quantify the contribution of sulfuric acid to the initial steps of the particle formation, we estimated the growth due to sulfuric acid in both 4-7 and 7-25 nm size ranges, GR_{4-7}^{SA} and GR_{7-25}^{SA}, respectively. Figure 6 shows the resulting sulfuric acid contribution to the total experimental growth rates at SNS and UGR. It is clear that sulfuric acid can only explain a small fraction of the growth rates retrieved in the ranges 4-7 and 7-25 nm at both measurement sites. The ratio GR_{4-7}^{SA}/GR_{4-7} is 9% at both stations, and the ratios GR_{7-25}^{SA}/GR_{7-25} are 0.8% and 1% at SNS and UGR, respectively. Thus, sulfuric acid explains similar small fraction of the experimental GRs at both sites during the study period and, despite a proxy sulfuric acid concentration was used here, these results strongly suggest a significant contribution of other vapours in this period at both sites. Furthermore, despite sulfuric acid is traditionally considered as one of the main factors for NPF events to occur, SO_2

and sulfuric acid concentrations are lower at SNS when events take place than on non-events days (figure not shown), indicating that sulfuric acid concentrations are sufficient for events to take place but not the factor that drives NPF events."

"When considering event and non-event days, the CS was higher on event days (2.9 and 6.7 × 10^{-3} s^{-1} at SNS and UGR, respectively) compared to non-event days (1.8 and 6.6 × 10^{-3} s^{-1} at SNS and UGR, respectively), indicating that CS does not play a significant role in NPF processes at both sites. It is worth mentioning that the role of CS in NPF processes differs from one high altitude site to other as Sellegri et al. (2019) pointed out. For example, Boulon et al. (2011) at Puy de Dôme station, Venzac et al., (2008) at the Nepal Climate Observatory Pyramid station and Lv et al. (2018) at Mount Tai found that higher CS inhibits the occurrence of NPF events. However, Boulon et al. (2010) at Jungfraujoch station, Garcia et al. (2014) at Izaña station and Rose et al. (2015) at Chacaltaya station found that higher CS observed in these sites does not inhibits the occurrence of NPF events. Overall, a detailed understanding of the role of CS in NPF events remains an open question and the chemical composition of CS could play an important role on the NPF processes (Tuovinen et al., 2020)."

3) P5, L26–28 and later P6, L15–17: The association of the three modes in the size distributions to size fractions should be proved by showing a typical size distribution and the size ranges. Does the position of the modes change in time at the sites? The authors may want to explain why they did not use modal areas from fitting, which was performed anyway, instead of size fractions.

In order to prove the association of three modes in the size distributions, Figure R1 shows the mean size aerosol distribution for the days presented in Fig. S2 of Supplementary Material. Figure S2 and Fig. R1 show that nucleation and Aitken mode are well separated at both sites with tinny contribution of accumulation mode as it is pointed in section 3.1 of ACPD manuscript. We agree that the use of modal areas is a useful information that gives information of aerosol dynamics and the processes involved on it. However, dynamics of aerosol size distribution has been studied in following sections using other parameters as growth rates. In addition, since the position of the modes will change on time, the use of modal areas from fitting makes impossible the comparison of aerosol concentrations at both sites.

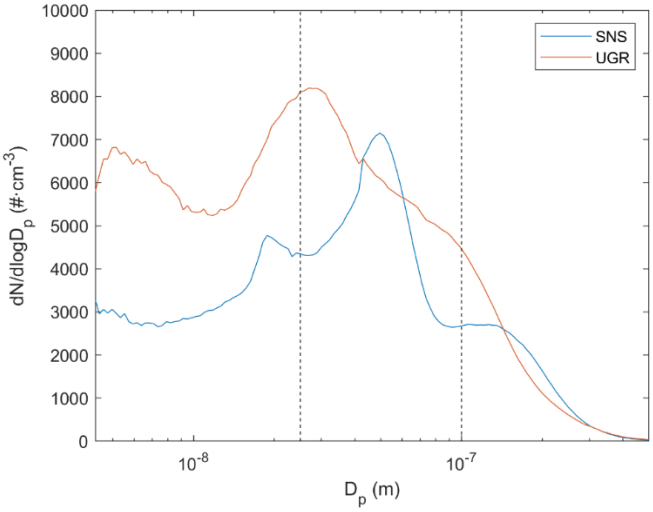

Figure R1. Example of diary mean aerosol size distribution at UGR and SNS sites.

The use of the aerosol size ranges presented in this work are commonly used to provide information about sources and atmospheric processing of particles (Hama et al., 2017 and references therein). In this sense, the nucleation mode (particle diameter < 25 nm) can originate from primary combustion particles emitted directly into the atmosphere and new particles formed in the atmosphere by gas-to-particle conversion. Aitken mode (25 nm < particle diameter < 100 nm) may include a mixture of soot particles emitted in combustion processes and coagulated nucleation mode particles. Accumulation mode particles (100 nm < particle diameter < 1000 nm) may be result from biomass and fuel combustion processes and coagulation and growth of Aitken mode aerosols by condensation of vapors onto existing particles. Therefore, the analysis of the mode-segregated particle concentrations can provide some information upon the sources and processes contributing to particle number concentrations.

In light of the above, we have included the following sentences in P6, L2–7 of new manuscript version:

"In order to gain some insight upon the sources and processes contributing to particle number concentrations over both sites, we segregated the 5-min particle size distributions measured by SMPS into three diameter ranges: nucleation mode from 4 to 25 nm (N_{4-25}), Aitken mode from 25 to 100 nm (N_{25-100}) and accumulation mode from 100 to 500 nm ($N_{100-500}$). This is because these distinct particle modes result from different emission sources and chemical and physical processes (e.g., Hama et al., 2017 and reference therein). In addition, total particle number concentration is calculated from the whole 4 to 500 nm range (N_{Tot})."

4) P5, L14–16: Further details on the "complete chemical analysis" should be given. What are the species measured, what are the analytical methods used and their performance properties?

We have made the following changes in the new manuscript version (P5, L17-21):

"The filters were conditioned and treated pre- and post-sampling and major elements (Al, Ca, K, Mg, Fe, Ti, Mn, P, Na) were determined by inductively coupled plasma mass spectrometry (ICP-MS) at Institute of Environmental Assessment and Water Research (IDAEA-CSIC, Barcelona, Spain) following the procedure of Querol et al. (2001). Detection limit and accuracy were estimated in 0.02 ng m^{-3} and 3% (Pandolfi et al., 2011). The concentrations of TiO_2 and Fe_2O_3 were indirectly determined on the basis of empirical factors (TiO_2 = Ti·0.6 and Fe_2O_3 = Fe·0.7)."

5) P6, L15–19: It is not completely clear what size interval do CoagSDp and NDp represent, and how they were calculated?

We have made the following changes in section 2.2 for better explanation:

formed in an NPF event. Thus, the growth rate (GR) is obtained as:

"$GR_{\Delta D_p} = \frac{dD_p}{dt} = \frac{\Delta D_p}{\Delta t}$ *Eq. (1)*

where D_p is the representative diameter of the NPF mode at time t. In this work, the growth rates in the range 4-7 ($GR_{4\text{-}7}$) and 7-25 nm ($GR_{7\text{-}25}$) were calculated. The uncertainties in the calculated GRs was estimated on 19% and 8% for the 3-7 and 7-20 nm size ranges (Yli-Juuti et al., 2011).

The formation rate (J_{D_p}) is defined as the flux of particles past the lower limit of the size range (ΔD_p), and it is obtained by adding up the observed change in the observed particle number concentration and the losses of particles due to coagulation and growth out of the size range (ΔD_p) and it is calculated following the methodology described by Kulmala et al. (2012):

$$J_{D_p} = \frac{dN_{\Delta D_p}}{dt} + CoagS_{\Delta D_p} \cdot N_{\Delta D_p} + \frac{GR_{\Delta D_p}}{\Delta D_P} \cdot N_{\Delta D_p} \quad \textit{Eq. (2)}$$

where the first term on the right hand side represents the rate of change of particle concentration with time (where $N_{\Delta D_p}$ is the particle number concentration in the size range ΔD_p); the second term describes the loss of particles due to coagulation with larger aerosol particles (where $CoagS_{\Delta D_p}$ is the coagulation sink); and the third term considers the growth out of the considered size range. The coagulation sink was calculated from the geometric mean of the considered size range (ΔD_p) to the upper SMPS diameter limit (500 nm), according to Kulmala et al. (2001). In this study, we calculated the formation rates at diameters (D_P) 4 nm (J_4) and 7 nm (J_7) using the diameter range (ΔD_p) of 4-7 and 7-25 nm, respectively."

6) P8, L18–19: How can you explain the high contribution of the nucleation mode (49%) to the total particle numbers on non-NPF even days?

This contribution at SNS and UGR sites are for the whole campaign. Despite it is not included in the manuscript, the contribution of nucleation mode aerosol concentrations is lower during non-event days at both measurement sites (~38% at both sites).

Minor comments:

7) Abstract and P3, L30 and L32: Abbreviation a.s.l. should be resolved.

Done

8) P5, L6: Abbreviations RH and PSL should be resolved.

Done

9) P8, L32: Rewording is required (in aerosol nucleation mode aerosol concentration).

Done

10) P9, L10–11: Repetition; it should be removed.

We agree and made the following change:

"The results of NPF classification (events, non-events or undefined and bad-data days) are summarised in Table 2."

References

- Ueda et al., 2016: Number–size distribution of aerosol particles and new particle formation events in tropical and subtropical Pacific Oceans.

- Pandolfi et al., 2011: Source apportionment of PM10 and PM2.5 at multiple sites in the strait of Gibraltar by PMF: impact of shipping emissions.

- Tuovinen et al., 2020: Investigating the effectiveness of condensation sink based on heterogeneous nucleation theory.