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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Increased new particle yields with largely decreased probability of survival to CCN size at the summit of Mt. Tai under reduced SO_2 emissions" *by* Yujiao Zhu et al.

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Anonymous Referee #4

This paper investigates long-term behavior of new particle formation (NPF) and associated particle growth at an elevated site. This is an important and scientifically very interesting topic, since there are quite limited number of studies about the response of NPF to SO2 emission reductions, and since the obtained results are somewhat mixed between different environments. The fact that the study is based on relatively short-term measurement campaigns made in different seasons, rather than continuous measurements over full years, limits the reliability of the obtained results, and this

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should be properly acknowledged in the paper. Anyway, I would support publication of this paper, provided that the authors will address the issues raised below.

Response: Thanks for the reviewer's comments. We agree that long-term continuous measurements would allow better investigating NPF trends under changing ambient conditions including air pollutants and meteorological factors. Due to practical difficulties, we tried short-term measurement campaigns made in different seasons of multiple years to characterize the NPF, with particular attention to the response of NPF to SO2 emission. The limitations of the non-continuous measures and the uncertainties to explain the results have been added in the revised discussion. We also try our best to respond the comments and revise our manuscript accordingly.

The introduction of this paper is generally well written. However, it would benefit from having a more concrete list of scientific questions aimed to addressed (in addition the aim mentioned on lines 75-76) in this paper. Two other, minor issues in this section: 1) the term "functions" on line 34 does not sound correct, perhaps "mechanisms"?, 2) the statement on line 74-75 is unclear. What altitudes are authors referring to here, above the boundary layer in general or upper free troposphere? One should be more careful with this, as elevated NPF can be associated with many different things, including convective uplift, presence of clouds, mixing of different air masses etc.

Response: Thanks. Lines 75-76 was revised as follow: "The main purposes of this study included: 1) to examine the effects of reduced SO2 emissions on the regional NPF events at high altitude (from the upper boundary layer to the lower free troposphere), i.e., changes in NPF frequency, intensity and the subsequent growth of new particles; 2) to quantify the potential contribution of new particles to the CCN population, and its changes under SO2 emission reduction; 3) to rationalize variation patterns of NPF characteristics and CCN parameters in terms of observational concentrations of gaseous precursors, their origins and atmospheric behaviors."

In the revision, we change ""functions" to "then raise up with different health and climate

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effects". On line 74, we change "at higher elevations" to "above the boundary layer in general".

We agree that convective uplift, presence of clouds, mixing of different air masses, etc., may affect NPF events in clean remote atmospheres. We revise our discussion on the light of the issue.

Experimental methods have been described very shortly, and should be expanded a bit. How were the measurement data used in the current paper quality checked, are these data undergoing any quality assurance procedures? Did detection limits etc. cause any issues for data interpretations? Were there any serious gaps in the data during the periods chosen for the current study?

Response: Agree. The information will be added in the revised manuscript as following:

The WPS instrument was calibrated and/or repaired every 1-2 years by its vendor. The calibration parameter including the DMA sample/sheath flow, LPS sample/sheath flow, DMA/CPC pressure, DMA voltage, and DMA/ambient temperature. Polystyrene Latex (PSL) spheres (NIST) with the mean diameter of 100.7 nm and 269 nm were used for calibration. The detection limit of DMA was 10 nm when the DMA sample flow and sheath flow were 0.3L/min and 3 L/min, respectively. The detection limit of DMA could shift down to 5 nm when the DMA sheath flow increased to 4L/min (advanced mode). However, the pump consumption was faster. In this study, the detection limit of DMA was 10 nm in 2007 and 2009, while it shifted down to 5 nm in 2014, 2015, 2017, and 2018. To be consistent, only concentrations of particles >10 nm were used for the analysis. At the beginning of each campaign, the zero-points of the DMA, CPC, and LPS were checked using a purge filter at the inlet. The WPS sometimes operated improperly and the data had been excluded in the analysis.

SO2, O3, NO and NO2 were continuously measured at the Mt. Tai station since 2007. We performed multi-point calibrations every month and changed the filter every two weeks. The detection limits of SO2, O3, NO and NO2 were 1 ppb, 0.4 ppb,0.04 ppb

and 0.4 ppb, respectively. PM2.5 was calibrated every three months by the method of mass foil calibration according to the instrument manual with the detection limit of 0.5 μg/m3. A multipoint calibration was performed for the online MARGA before and after the field campaigns in order to examine the sensitivity of the detectors. The detection limits were evaluated as 0.05, 0.05, 0.04 and 0.05 μg m$-$3 for Cl-, NO3-, SO42- and NH4+, respectively. More details about the instrument calibration can be found in Wen et al., (2018) and Li et al., (2020).

Concerning the calculation methods, the authors should explicitly mention in main text (section 2.2.1) at which size particle formation rates were calculated, and what size range the calculated particle growth rates refer to (or if the applied size range for this calculation varied from event to event). Also, definition of "NPF duration" referred to e.g. on line 298 should explicitly described. Is it the time period over which new particles are observed to appear at the smallest sizes, or the time period over which the growth of new particle to larger sizes can be followed.

Response: Thanks. In the revised manuscript, we added “The apparent formation rate of new particles is calculated based on the nucleation mode particles in sizes of 10-25 nm. The apparent growth rate is quantified by fitting the geometric median diameter of new particles (Dpg) during the whole particle growth period. The size range of Dpg varies from event to event. Details of the calculation equations can be found in the supplementary materials.”

The definition of "NPF duration" has been added and reads as “The initial time of an NPF event was defined as the new nucleation mode particles started to be observed. The end time of an NPF event was normally determined by the new particle signal dropping to a negligible level and the total particle number concentrations approaching the background levels before the NPF event. In cases with the invasion of other plumes, the end time was determined by the new particle signals being suddenly overwhelmed by plumes and can’t be identified since then. The NPF event duration was defined as the time duration between the initial time and end time of an NPF event. Noticed that

the detection limit of WPS was 5 nm or 10 nm, but the particles were nucleated at the critical cluster sizes around 1-1.5 nm. Thence, the NPF should occur for some times prior to our observation, and the actual duration should be longer than our calculation."

Categorizing NPF event based on the maximum size that the formed particle are able to reach by growth is in principle fine. However, doing that has one important issue that should be at least mentioned, and preferably shortly discussed, in the text. Following particle growth over several days, or event over the night, from observations is often difficult because of the typically large diurnal variation of boundary layer properties (e.g. mixed layer height), and because of changes in measured air masses. This can be seen, for example, on Dec 24 NPF event shown in Figure 1a: there are at least two major discontinuities in the particle number size distribution data (apparent in sudden huge changes in particle number concentration in certain size ranges). As a result, it is highly questionable whether the particles observed to reach 217 nm actually initiated from the NPF event that took place much earlier on Dec 24. The same issues concerns the use of the term SP (survival probability). SP works fine when following the particle growth for a few hours, but becomes questionable for larger time periods. The authors should replace the term "survival probability" with something like "apparent survival probability" and discuss shortly this issue in the paper, including when interpreting the results.

Response: In this study, Dpgmax and SP were calculated within the NPF duration. The definition of NPF duration has been clarified in the response above and will be added in the revision. In addition, a few spikes were excluded in calculating Dpgmax and SP since the spikes were characterized by a sudden change in particle number size distribution (PNSD) and may reflect the intrusion of primary or aged plume signals.

As reported in numerous literatures, NPF was a regional phenomenon occurring in a spatial extent varies from tens to thousands of kilometers (Kulmala et al., 2012, Nat. Protoc.) However, it is almost impossible to occur identic NPF events over the large spatial range because of different concentration levels of nucleation precursors. In

reverse, spatial heterogeneity of regional NPF events is a common phenomenon and would cause the discontinued PNSD to some extent at a fixed observational site.

No criteria have been well-established in the literature to identify spatial heterogeneity of NPF events. In this study, spatial heterogeneity of NPF events was assumed for the discontinued PNSD if no intrusion of primary or aged plume signals were clearly identified. Even though the intrusion of primary or aged plume signals overwhelmed new particle signals for a short period, new particle signals can still be reasonably observed afterwards in the contour plotting. The discontinued PNSD was also assumed as the continuity of the NPF event. The NPF event on Dec. 24 was illustrated as example:

On the Dec. 24 event, (Figure R1), the two discontinuities appeared at 7:00-9:00 and 16:10-18:50 on Dec. 25. From 22:48 on Dec. 24 to 7:00 on Dec. 25, N10-300nm continuous decreased from 1.1$\times$104 cm-3 to 0.8$\times$104 cm-3, meanwhile, Dpg grew from 30 nm to 63 nm with the growth rate of 4.0 nm/h. Between 7:00 and 9:00, N10-300nm and Dpg oscillated at 0.8$\pm$0.1$\times$104 cm-3 and 51$\pm$6 nm. At 9:00, N10-300nm went back to 0.8$\times$104 cm-3 and Dpg was 72 nm. In these two hours, new particles were hypothesized to experience a growth similar to the previous curve. Similarly, Dpg was 115 nm at 16:10 and 128 nm at 18:50. The assumed growth rate during the 2.7 hours was about 4.8 nm/h, close to the previous GR. Actually, when we fitted the entire Dpg between 22:48 on Dec. 24 and 18:50 on Dec. 25, the GR was 4.9 nm/h and R2=0.97, suggesting that particles grew in a smooth curve.

In this case, Dpg reached the maximum of 163 nm at 9:00 on Dec. 26, then the new particle signal was overwhelmed by pollutant plumes. ΔNCCN reached the maximum at 20:23 on 25 Dec. The SP was calculated as SP = ΔNCCN/NMINP, and SPCCN50, SPCCN80, and SPCCN100 was calculated to be 0.2, 0.2 and 0.15, respectively.

We agree to change “survival probability” to “apparent survival probability”. The judgment of spatial heterogeneity in other NPF events followed the similar approach above, and we will add the discussion of spatial heterogeneity in the revised manuscript.

The authors should be a bit more careful when using the term "trend". On line 191, for example, should there read "pattern" rather than “trend”? Multi-year trends can be season-dependent, but I suppose this not what the authors mean here. Please check out that "trend" is correctly used throughout the paper.

Response: Thanks. We agree the reviewer’s comment that "trend" was inappropriate in this paragraph. Our main purpose was to examine the effects of reduced SO2 emissions on the regional NPF events characteristics and the CCN parameters. We will change “trend” to "pattern" in this sentence and go through the full text and revise the ambiguous statements.

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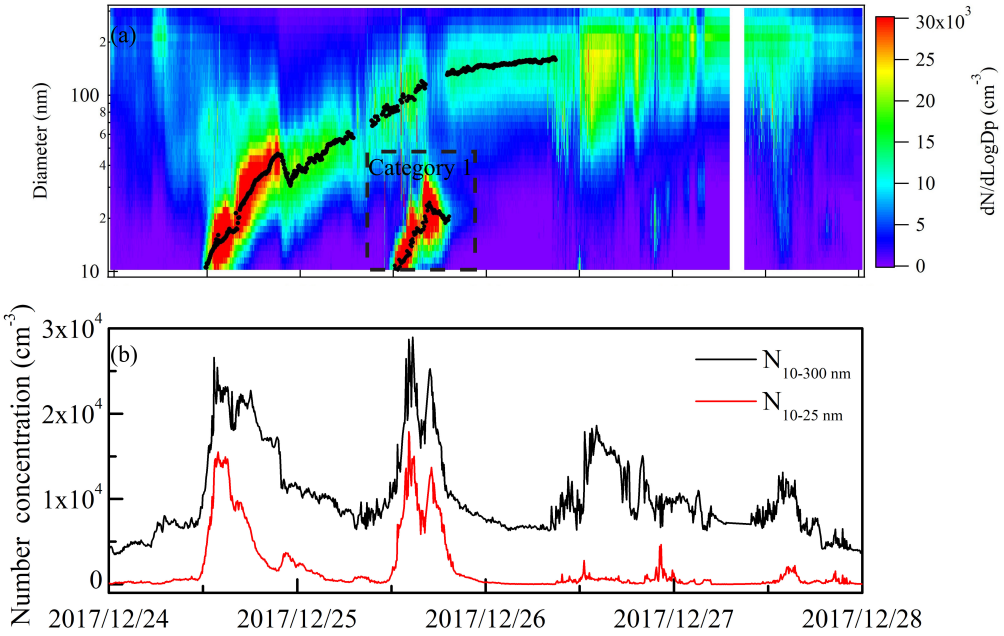

Fig. 1. Figure R1 Contour plot of NPF events (a) and the time series of particle number concentration in 10-25 nm (N10-25nm) and 10-300 nm (N10-300nm) (b) during 24-27 Dec. 2017.

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