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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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Response to Anonymous Referee #3

The manuscript analyzes seven field campaigns where particle number size distributions (PNSD) and sulfur dioxide were measured at the summit of a mountain site in the North China plain. Supporting measurements of time-resolved PM2.5, O3, and oxides of nitrogen were taken. And each campaign included 1-h time resolution ions in PM2.5 using water extractive methods (URG-AIM or MARGA). The most recent campaign was in 2018. Across the 7 campaigns, a little over 100 particle formation and growth events were detected, with the analysis focused on the size range of 10-300 nm size

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range. From the earliest to most recent campaign, SO2 emissions and concentrations have dropped dramatically, and the paper tries to analyze whether the particle formation and growth activity has changed in ways that are expected from the sulfur dioxide decrease. A large number of metrics are computed and then analyzed for each particle formation and growth event (PFGE). The metrics include, but are not limited to, the apparent formation rate of 10-25 nm particles (FR), the growth rate, the absolute increase in N10-25 particle concentration from the start to the peak of the PFGE (this is the NMINP variable), the PFGE duration, the PFGE frequency, the size to which the growth event reaches (Dpgmax variable in the manuscript), and particle counts which are used as surrogates for the change in CCN concentrations at low, medium, and high supersaturations (N100-300, N80-300, and N50-300). The paper includes values for and discussion of total VOC during the campaigns.

Complicating the analysis is that the field campaigns were in different months of the year: April 2007 (∼30 d), June 2009 (∼20 d), Aug 2014 (∼30 d), Oct/Nov 2014 (∼70 d), Jul 2014 (∼40 d), Dec 2017 (∼35 d), and Mar 2018 (∼30 d).

The paper's abstract makes five claims: a. The formation rate in 2018 is 2-3 times higher than the formation rate in 2007. b. Net maximum increase in nucleation mode number concentration is 2-3 times higher in 2018 than in 2007. c. The occurrence of events where the mode of the growth event goes above 50 nm is lower in 2018 than it was in 2007. d. A surrogate for CCN production at high supersaturation (N50-300 at its peak during each growth event minus N50-300 before the event) decreased from 3703 per cm3 (before 2015) to 1026 (2017-2018). e. The authors argue availability of organic precursors has increased in the most recent campaigns, allowing more particle production and initial growth; furthermore, they argue that the lack of later growth is from reduction of "anthropogenic precursors" (presumably SO2).

The paper requires substantial revision before it is suitable for publication. The key issue, to this reviewer, is that making accurate claims about year-on-year trends and variability in PFGE is difficult. The requirements to make the claims defensible are:

(1) take a sufficient number of samples to reduce random variability and give sufficient statistical power; (2) take steps to minimize, test for, and quantify campaign-specific systematic instrument bias (also known as “instrument drift”); (3) take steps to enforce consistency in any subjective data interpretation steps, such as classification of PFGE into “types” and the determination of the start and end times of events; (4) use statistical methods designed for trend analysis, time series analysis, and combined analysis of seasonal and interannual variability.

Each requirement needs to be met in order for the claims about trends to be defensible. And for peer review and reproducibility purposes, things need to be documented for the peer-review and scientific communities.

I think the current work fails to meet all four of the requirements. While some of the conclusions are likely accurate (in that they would not change if all the requirements were met) – others would change, or require extensive qualification.

Response: Thanks for the review’s constructive comments. We agree that some analyses and related conclusions in our original version should be more conservative. In addition, more clarifications are needed to better defense them. Scientific community normally prefers to see the extracted trend in ambient variables using the measurement data over 20 years. Thus, the technical term “trend” used in the original version is problematic and should be removed.

Long-term continuous measurements may allow better investigating NPF trends, however, all statistical tools in literature suffer from the weakness to some extent in extracting the de-weathered trend in interested variables associated with anthropogenic perturbation, based on our previous studies. For non-continuous measurements, it is still a common challenge to address specific scientific questions using the proper statistical analysis. We agree that the weakness and challenge should be included in the revision.

A comparative analysis was conducted to study particle formation and growth events

(PFGE) in different years based on two observational facts, 1) their occurrence frequencies in 2007 and 2009 were reasonably same as those in 2017 and 2018 even in different seasons; 2) a large decrease in SO2 mixing ratio 2017 and 2018 against in 2007 and 2009. We then focused on comparative analyzing the spring PFGEs in 2007 and 2018, where uncertainties from varying ambient factors may have been largely minimized. This will be clarified in the revision. Moreover, an on-site automatic weather station has been operated continuously since 2005. Meteorological parameters such as temperature, relative humidity, wind speed, wind directions and pressure will be analyzed statistically to facilitate the discussion of PFGEs during the seven campaigns.

We also found a large variation in occurrence frequency of summer PFGEs in different years. For the summer PFGEs, it may require extremely abundant chemical information to study the effect of decreasing SO2 levels on PFGEs because of a huge perturbation from meteorological conditions and related biogenic emissions of air pollutants. On the other hand, the observations of summer PFGEs also implied that the same occurrence frequencies of PFGEs may be a critical indicator to constrain the comparative analysis.

We highly appreciate the comments on technical issues of measurements. The commercial instruments were routinely calibrated to ensure the QA/QC using the service provided by their vendors. We agree that more cautions should be paid to instrument limitations, especially in a small particle size range. In the following text, we will try our best to address the comments point by point and revise the manuscript accordingly, in order to improve our analysis more defensible and robust.

1. Statistical power:

PFGE exhibit substantial seasonal variation, due to changes in temperature, relative humidity, biogenic activity, atmospheric chemistry, soil moisture, preexisting aerosol concentration and chemistry, radiation, cloudiness, boundary layer structure, land cover/vegetation canopy structure, synoptic meteorology, anthropogenic emissions, and atmospheric ion levels. Local meteorological features (i.e. orographic meteorol-

ogy) and local sources may also have month-to-month variability. And at the 20-30 d time scale, large scale persistent geophysical features can cause a whole campaign of measurements to be atypically high or low for a number of PFGE variables. To accommodate all these sources of variability, large sample sizes are required for analysis of seasonal variation and interannual trends. In the absence of large sample sizes, careful pairing of events and analysis of alternate sources of variability / alternate hypotheses are needed isolate cause-effect relationships on specific PFGE variables.

With each campaign at a slightly different time of the year, some campaigns as short as 20 d, and no discussion of whether air pollution levels, air pollution meteorology, and climate variables were at climatologically representative levels, the reader has to apply great skepticism to any claims of interannual trends and cause-effect relationships for those interannual trends. See for example (Birmili and Wiedensohler 2000) who do take into account air mass characteristics.

Response: To our best understanding from recent review papers on PFGE, eight variables, i.e., concentrations and cumulative generation amounts of sulfuric acid together with Highly Oxygenated Organic Molecules (HOM) and other secondary organics in different volatilities, the product of gaseous HNO3 and gaseous NH3 minus the equilibrium constant of NH4NO3 and then minus the kelvin effect term, cumulative generation amounts of condensed NH4NO3 on size-dependent particles, would directly affect apparent new particle formation rate (FR), apparent net maximum increase in the nucleation-mode particle number concentration (NMINP), new particle growth rate (GR) and the maximum geometric median diameter of grown new particles (Dpgmax). Although gaseous amines have been proposed to participate in ambient nucleation, their concentrations in China, based on the authors' work, are too high (relative to sulfuric acid) to act as the limitation factor. How aminium salts contribute the growth of newly formed particles larger than 10 nm, which is the one of focus in this study, is poorly understood in China. What the reviewer claim above may indirectly affect the eight variables to some extent. Only the information of the eight variables is not suf-

ficient to support our analysis, those indirect factors should be cautiously utilized to facilitate the analysis. The argument will be added in the revision.

We agree that the technical term “trend” is misleading and will be removed in the revision. We will also revise our discussion on the cause-effect relationships of PFGE by considering significant changes in the eight variables. If the required data are not available, we tried to use indirect factors facilitate analysis.

In polluted and NH3-rich (we may reasonably assume that amines may also be rich relative to sulfuric acid) ambient air in China, the influence of air mass characteristics on PFGE may be totally different from that in the clean and pristine atmospheres. In clean and pristine atmospheres, air mass characteristics may provide important information on precursors’ sources of PFGE. In China, precursors of PFGE are abundant in general. For example, the occurrence frequency of PFGE reached ~50% in winter campaign as presented in this study, while the value was less than 5-10% in winter in Europe. Alternatively, air mass characteristics greatly affect moisture characteristics and may subsequently affect the cloudiness (radiation) and H2SO4 concentration through modulating OH free radical concentration. Of course, the latter is poorly studied so far.

The size distributions shown in Figure S3 are suggestive of insufficient number of days sampled in the dataset. Telling whether the system shifted from unimodal to bimodal behavior between 2015 and 2017 (all unimodal for 2015 and prior) vs. this occurring through some instrument drift vs. this occurring through sampling non-climatological conditions due to small samples sizes is difficult.

Given the decrease (Table 2) in PM2.5, sulfate, and SO2 between spring 2007 and 2018 (PM2.5 60 vs. 30 ug/m3; sulfate 17 vs. 4 ug/m3, SO2 18 vs. 3 ppb), more discussion is needed of the large increase in condensation sink in 2018 (Figure S3) and in the large increase in the height of the size distribution function at 100 and 150 nm between 2007 and 2015.

The discontinuity in the slope of the size distribution function at 200 nm also indicates there may be some drift in the size-specific performance of the WPS (Figure S3). The discontinuity in slope is not really evident until 2017, but then appears in 2017 and 2018.

Response: We agree that the analysis of PFGE in the origin version misses out the important point. On the light of the comments, we re-checked the data. We do find that three channels in WPS around 213 nm suffered from unexpected errors in reporting number concentrations in approximately 30% sampling days in 2017 and 2018. It has a minor influence on PFGE in 7 NPF days out of the total of 32 NPF days in 2017 and 2018 as shown in Fig. S3. The data in the three channels suffering from abnormal errors will be corrected by assuming a linear decrease of particle number concentration from 150 nm size bin to 300 nm size bin. Thank again.

We plotted particle number size distributions on non-NPF days in different years (Figure R1). Bimodal particle number size distributions can be observed in 2009, 2014 and 2015. We don't see any shift when the size distributions in 2014, 2015 and 2018 were compared with each other. We also find that the median geometric diameters of accumulation mode on NPF days in 2017 were consistent with those on non-NPF days in 2014, 2015 and 2018. However, the median geometric diameters of accumulation mode on non-NPF days in 2017 did shift to the large size and the same was true for those on non-NPF days in 2009. Moreover, the median geometric diameters of accumulation mode on NPF days in 2009 were consistent with those on non-NPF days in 2014, 2015 and 2018. Overall, our regular instrument maintenance appears to be effective to prevent from the instrument shift, except the occasional problem at three size bins around 213 nm.

In the origin manuscript, we calculated condensation sink based on the different size range of particle in 2007 (10-153 nm) and 2018 (10-300 nm). To be consistent, we recalculated CS based on 10-153 nm particles on 2018, and the average of 0.4$\pm$0.15 s-1 was slightly larger than the average CS in 2007 (0.32$\pm$0.19). CS should be unrelated

to secondary particles via ambient nucleation since the particles cannot grow over 60 nm. Primary emissions of the accumulation mode particles were out of scape of this study, although they may scavenge precursors of PFGE to some extent.

2. Minimize, test for, and quantify campaign-specific instrument drift:

Achieving consistency in PNSD in long-term measurements is difficult. And it is not sufficient to state that each individual campaign had sufficient quality assurance, referring the reader to the campaign specific papers. There needs to be a presentation of data and discussion of how comparable the instrument responses are from campaign to campaign. What steps were taken to make sure instruments were not drifting. Aging of components can cause variation in flows, sizing accuracy, counting accuracy, particle losses, CPC supersaturations, and in the effective lower size limit of the instrumentation of the particle number spectrometer system. The detection efficiency as a function of size at the lower range of the instrument (5-25 nm), at the upper range of the mobility analyzer, at the lower end of the optical particle devices, and at the upper end of the optical particle analyzer – these are all difficult to maintain at stable levels over long periods of time. The total particle counts, height of the size distribution function, sensitivity at the lower and upper ranges of size distributions – these vary from year to year and require careful intercomparison, quality assurance, and maintenance procedures to deal with. See for example the results of intercomparison studies (Pfeifer, Müller et al. 2016) and papers focusing on quality assurance, calibration, and harmonization (Pitz, Birmili et al. 2008, Wiedensohler, Birmili et al. 2012, Wiedensohler, Wiesner et al. 2018, Gaie-Levrel, Bau et al. 2020). Comparison to other instruments for total particle counts, size distribution functions in overlapping regions, checks with monodisperse particles are some of the techniques that can be used to establish more confidence and quantify campaign-to-campaign comparability.

Consistency in inlet dimensions, inversion algorithms (including multiple charge correction), use of impactors to manage multiple charge issues, corrections for inlet transmission efficiency, – these can all be issues in campaign-to-campaign comparability.

They need to be discussed.

While being able to reproduce time-resolved PM2.5 measurements from the WPS size distribution is not sufficient to show accuracy in the nucleation and Aitken ranges – it is probably necessary. At least showing consistency from campaign to campaign in the volume of particles measured by the WPS and the mass of particles by time resolved mass measurements can help to demonstrate stability in instrumentation and data processing algorithms.

The fact that the authors are using an instrument with nominal lower cutoff of 5 nm, but discarding data between 5-10 nm indicates that there may be a problem with sensitivity at the lower size limit, or (more likely) variability in the sensitivity at the lower size limit. There is further evidence in Figures 1 and S6 – of a problem. In all the bursts shown save one, the particle size distribution function slopes down from a peak at about 13 nm to a lower value at 10 nm. If the instrument is biased low in the 10-13 nm range, then the statistics developed in the work will also be biased. If that bias varies from campaign to campaign, then that creates additional interpretation difficulties.

At line 180, it is implied that at times the WPS was collocated with instruments with lower limit of 3 nm. Therefore, the actual performance in the 5-15 nm range could (and should) be determined though comparison to such collocated instruments.

Response: Honestly, we rely on the instrument vendor on instrument maintenance and calibration every 1-2 years. Except the problem at size bins around 213 nm sometimes occurring in 2017 and 2018, the measured size distributions were reasonably consistent as mentioned above. We excluded the concentrations of particles below 10 nm for analysis in order to keep the lower limit of PNSD consistent in seven campaigns. More details are presented below.

In revision, we will add the information 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."

In addition, the aging of components may lower the detection efficiency of WPS. However, the increased FR and NMINP in 2017-2018 reveal that the signals of nucleation mode particles enhanced in recent years. As presented in original manuscriptïijŇit reads as"During the four campaigns in 2007, 2009, and 2014, the calculated FR varied narrowly in each campaign and the campaign average narrowed to 0.8–1.2 cm^{-3} s^{-1}. The FR increased thereafter, i.e., 2.6 $\pm$ 1.3 cm^{-3} s^{-1} in 2015, 2.0 $\pm$ 1.7 cm^{-3} s^{-1} in 2017, and 3.0 $\pm$ 2.7 cm^{-3} s^{-1} in 2018."Therefore, we convince that the instrument maintenance can effectively reduce the aging impact of instrument components on observational data.

Conductive tubes (TSI 1/4 in.) were used for the WPS sampling in each campaign. The length of the tube was kept at about 2 m in each campaign (fixed position of WPS in the container). We used the SWS mode (DMA operating in the voltage-scanning mode) for measuring. The charge correction was calculated by the Boltzmann charge distribution, and the equation has been considered in the instrument algorithm.

PM2.5 were measured in 2007, 2014, 2017 and 2018. Assuming the particle density is 1.5 g cm-3, the mobility diameter can convert to aerodynamic diameter following the equation of Aerodynamic diameter=Mobility diameter$\times\sqrt{1.5}$. The particle mass

concentration in each size bin can be calculated according to the particle number concentration reported by WPS. Then we integrated the mass concentration of less than 2.3 μm in aerodynamic diameter (1.9 μm in mobility diameter) and compared with the PM2.5 mass concentration reported by TEOM 1400a (2007) or Thermo 5030 SHARP (2014-2018). The relationship of hourly average data is showed in figure R2.

In 2007, we calculated the mass concentration of PM0.18 from WPS and found it has a weak correlation with PM2.5. A slope of 0.05 indicated that the particles we observe account for a minor fraction of the total mass. In the two campaigns in 2014, the mass concentration of WPS-derived PM2.3 and SHARP measured PM2.5 showed good correlations, with slopes of 0.69-0.76. In 2017 and 2018, we removed the abnormal data in three bins around 213 nm, and found a good linear correlation between the two methods, but the slopes slightly increased to 0.86-0.9. It should be noted that our calculation method depends on the density of particles. If the actual particle density deviates from the assumed value, the integrated volume (mass) is misadjusted. The difference in slopes may be due to the difference in particle density, or other unknow factors. Nevertheless, all of the deviations were less than 30% and within a reasonable range, and the linear correlations are generally good. Thus, our result showed the WPS was generally stable during the four campaigns. These will be added in the revised supplementary.

As we mentioned above, 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. On April 7 (figure 1b), the initial peak at about 13 nm. That because the initial nucleation was influence by sporadic spikes, which overwhelmed the nucleation signal. In revision, we will remove the fitted Dpg when the PNSD was influenced by spikes.

The measurements made by NAIS at Mt. Tai were reported by Lv et al., 2018. But we have no confidence on the raw NAIS data. Fortunately, we have conducted a comprehensive comparison between the WPS and a SMPS (GRIMM, Germany) at a

costal site in Qingdao, China. The SMPS consists of a DMA (55-UïijŇGRIMM) and a CPC (5416ïijŇGRIMM). It covers the particle size range of 10 nm-1000 nm, and is set up to 127 channels. The time resolution of SMPS is 4 min. The two instruments of WPS and SMPS were operated side by side during 2-7 July 2020 for intercomparison.

Figure R3 shows the comparison of particle number concentration in the range of 10-25 nm (nucleation mode) and 10-300 nm (particle size range we used for calculation in this paper) between WPS and SMPS. Particle number concentration in these two size ranges showed good linear correlations, suggesting the measurements of the two instruments are highly consistent. Furthermore, the highly correlated data indicates that the WPS is not experiencing aging problems.

3. Consistency in subjective data interpretation/classification steps:

It is not clear which of the variables used for analysis involve human classification. Sometimes, human classification is used for PFGE types (often using how smooth the growth event is in time); human classification is used sometimes for establishing times (start of event, end of the event). The end time is described. From line 113 of manuscript, “The end time of an NPF event was defined as the time when the particle number concentrations approached the background levels observed before the NPF event. The NPF event duration was defined as the time duration between the start time and end time of an NPF event.” This seems like the end of event was a subjective determination of when background was approached. Thus the end time, duration, and any rate that has the duration in the denominator may be subjective.

For subjective (human) event classifications, were the events uniformly reclassified for this paper, or were prior classifications adopted from 2007 and 2009 and mixed with new classifications done for the more recent campaigns. See (Dal Maso, Kulmala et al. 2005) for best practices on human classification.

Response: In revision, we will add the details when classifying NPF events: “In this study, particles with diameter smaller than 25 nm were defined as nucleation mode

particles (Kulmala et al., 2012). Followed the criteria proposed by Dal Maso et al. (2005) and Kulmala et al. (2012), three features had to be met to classify an NPF event: 1) a distinctly new nucleation mode particles must appear in the size distribution; 2) the new mode should prevail over a time span of hours; 3) the new mode should show signs of growth. All three features are required for a day (00:00-23:59 LT) to be classified as an NPF day. Otherwise, the day is classified as a non-NPF day.

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."

Followed the definition above, we classified the NPF event uniformly during the seven campaigns, i.e., from 2007 to 2018.

4. Statistical methods appropriate to analysis of combined seasonal and interannual variability

Statistical procedures for evaluating trends in seasonally varying time series need to be followed in order to state claims that trends exist. These can be found in a number of textbooks, papers, and government reports. See for example Statistical Methods for Environmental Pollution Monitoring by Gilbert https://www.osti.gov/servlets/purl/7037501/. And (Asmi, Coen et al. 2013, Collaud Coen, Andrews et al. 2013, Squizzato, Masiol et al. 2019). Many other good mod-

els for seasonally adjusted trend detection can be found in the O3, NOx, PM2.5, and hydrology/climatology literature. Squizzato et al. (2019) for example have the statistical procedures necessary to detect turning points (see line 236 where manuscript discusses turning points)

See for example line 290 “the CS still increased in 2018 compared with that in 2007.” That implies annual average condensational sink increased, and this is a season or month specific result – and it is not clear there is enough statistical confidence to state this. Many other locations in the paper have broad statements about PFGE behavior in one year vs. another, or imply a long term trend where it has not really been shown.

Interpretation of PFGE data from this site seems more complicated than most, because of two issues: (1) it is sometimes influenced by boundary layer and other times by free troposphere; (2) very long PFGE events (see for example Figure 1a, where a 3-d long event is shown) are being compared with shorter (midday + afternoon) growth events. See Figure 7 which has events ranging from 3-h duration to 85-h duration. The flow patterns and chemistry required to sustain a 3-h event and an 80+ h event are likely very different, and would require more thoughtful comparison metrics than used in the paper.

The paper acknowledges this difficulty in interpretation (line 295) but more needs to be done than just acknowledge the difficulty. See analysis papers from PFGE studies at other high altitude sites. They do attempt to determine the degree of FT influence and the impact of polluted boundary layer air. And there are many papers that factor in air mass characteristics and/or back trajectory in analysis of PFGE.

See for example Figure 1a where on 25-Dec 2017 there were simultaneously occurring a short PFGE (category 1) and evolution of the category 3 event that started on 24-Dec 2017. This raises a number of questions on how such a dataset can be analyzed to determine trends.

How much of the variability in data is that some campaigns had more free tropospheric

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influence and others have less. How much of the conclusions of the paper are driven by switches (during PFGE) in air mass influence to/from FT influence. In other words, PFGE events that have their evolution dynamics controlled by airflows, and not by chemistry – hence the authors observed lack of influence or counterintuitive effects of SO2.

As for statistical procedures, I think it would be much more appropriate to put 95% confidence intervals on means rather than standard deviations on the plots. (Most figures have standard deviations)

Some of the variables appear to NOT be normally distributed (see figure S4) and thus use of statistical tests designed for normally distributed data are inappropriate.

Another weakness of the approaches used are that changes in boundary layer height are not accounted for. This weakness cannot really be addressed without additional measurements, but it should be noted.

Response: We acknowledge that the technical term “trend” is misleading in the origin manuscript. It will be removed in the revision. The “turn point” was inappropriate and we will remove this in revision.

Line 290 will be changed to “Note that the campaign average of PM2.5 mass concentration in 2018 indeed decreased. The decrease was apparently determined by the decrease in >153 nm particles, since no significant difference existed in the CS (calculated based on <153 nm particles) between in 2007 and 2018.” We didn’t imply the annual trend of CS or other variables, we will go through the full text and revise the ambiguous statements.

Here we comprehensively analyze four cases of NPF events in different categories (category 1 events on 5 April 2007 and 6 April 2018, category 2 event on 8 April 2018), and category 3 event on 23 April 2007) in 2007 and 2018. The meteorological parameters, gases pollutants, PM2.5 mass

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concentrations and planetary boundary layer height (PBLH, download from https://goldsmr4.gesdisc.eosdis.nasa.gov/data/MERRA2/M2T1NXFLX.5.12.4/) were showed in figure R4 and R5. PBLH shows obvious diurnal variations, and the maximum value are 4110 m, 3000 m, 2316 m, and 2224 m on 6 April 2018, 7 April 2018, 5 April 2007, and 23 April 2007. There was no significant difference in the evolution of PBLH among the three categories. We argued that PFGE events were controlled by chemistry, since the changes of airflow always associate with the changes of air pollutant, which directly influence NPF as mentioned in the response to the first comment.

As reported in numerous literatures, the growth of newly formed particles is mainly attributed to sulfuric acid, ammonium nitrate, and secondary organic compounds (Wiedensohler et al., 2009; Riipinen et al., 2011; Zhang et al., 2012; Ehn et al., 2014; Man et al., 2015; Wang et al., 2015; Burkart et al., 2017; Lee et al., 2019; Wang et al., 2020). We therefore explore their respective contributions as follows. First, we calculated the contribution of sulfuric acid to the growth based on the observed mixing ratio of SO2 and equations 2-3 in section 2.2.2. Second, we examined whether NH4NO3 freshly formed in PM2.5 during the particle growth period. In case of no NH4NO3 formation, its contribution would not be expected. This is because an even higher product of HNO3gas*NH3gas is required to overcome the kelvin effect and form NH4NO3 in nucleation mode and Aitken mode particles. Thus, the growth unexplained by sulfuric acid should be mainly contributed by organics. In case of NH4NO3 formation, we considered the net increase in NH4NO3 may contribute to the particle growth, even though the ratios of increased NH4NO3 in PM2.5 may not be the same as the ratios in nucleation mode and Aitken mode particles.

On 6 April 2018 (category 1), the NPF event was first observed at 09:10. Dpg was fitted as 13 nm at 09:45, and continuous grow to 30 nm at 18:10. Then both of the particle number concentration and particle diameter decreased, and the plume overwhelm the new particle signal at 6:00 on 7 April. During the NPF period, sulfuric acid was esti-

mated to contribute about 16% to particle growth. The mass concentration of nitrate in PM2.5 was less than 1.0 μg m-3, implying that fresh NH4NO3 formation did not occur. Thus, the growth unexplained should be mainly contributed by organic matter.

On 7 April 2018 (category 2), Dpg increased from 13 nm at 10:00 to 43 nm at 18:00, then Dpg fluctuate at 41 nm-52 nm in the following 10 hours. Sulfuric acid was estimated to contribute about 11% to particle growth. The mass concentration of nitrate in PM2.5 continuously increased from 0.8 μg m-3 at 10:00 to 2.7 μg m-3 at 20:00, then decreased to 2 μg m-3 at 4:00 on 8 April 2018. Formation of ammonium nitrate seems to contribute to the growth of new particles in this case.

Similarly, on 23 April 2007 (category 3), sulfuric acid was estimated to contribute about 23% to particle growth. The mass concentration of nitrate in PM2.5 increased from 1 μg m-3 to 10 μg m-3 during the particle growth period, indicating its important role in the particle growth. On the contrary, the mass concentration of nitrate and sulfate decreased during the NPF period on 5 April 2007 (category 1), and new particles didn't grow to the larger size.

We summarized the mass concentration of SO42$-$, NO3$-$, NH4+ and OC during the formation and growth period of NPF events in 2007 and 2018 campaigns (added in Table 2). During the growth periods, the contribution of H2SO4 vapor to particle growth decreased from 36% in 2007 to 11% in 2018. The mass concentration of nitrate in PM2.5 also decreased from 7.4 $\pm$ 4.8 μg m-3 in 2007 to 6.7$\pm$ 5.5 μg m-3 in 2018. In addition, OC in PM2.5 was lower in 2018 (5.5 $\pm$ 2.0 μg m$-$3) than in 2007 (6.1 $\pm$ 3.0 μg m$-$3). In 2018, the reduced H2SO4 vapor, nitrate and OC formation may lead to the decrease in the growth probability of new particles. However, large uncertainties still exist because of a lack of data on the chemical composition of these smaller particles.

Figures 3 and 5 will be changed to the box chart with 95% confidence intervals on means.

Two sets of data in figure S4 are not linear correlated, and we will remove the four fitting

equations.

Other issues:

5. The abstract overstates the conclusions of the work. The conclusions have significant caveats, are based on limited number of sampled days, but the abstract makes it seem like the trends are well established, statistically significant, and based on a complete multi-year time series.

Response: Thanks. We will remove the “trend” in revision and rewrite abstract.

6. There are a number problems with Figure 6. It is not appropriate to grey out datasets that are not correlated. Data are data, and data points should not be deemphasized visually just because they do not fit a linear correlation. The datasets should be clearly labeled so that each symbol type can be connected back to its underlying study and land cover type. Having a linear correlation shown and then a change in the tick mark spacing is not a fair way of graphing in my opinion. The size ranges in question should be included in the axis labels and/or the caption. I believe this is the formation rate at 10 nm, and the NMINP at 10-25 nm? Is that consistent for all the datasets? If not, then I don’t think this is a fair plot to put in. I don’t think having regression equations and correlation coefficients on graphs is effective or appropriate (see additional comments on this later).

Response: Thanks. We have changed the grey markers to black, as shown in figure R6. In this study at Mt. Tai, all of the FR and NMINP are linearly correlated, and FRs were less than 15 cm-3s-1 (blue markers in figure R6). Therefore, the linear relationship was the key point we would like to address, and we change the tick mark space when FR larger than 20 cm-3s-1 in order to emphasize our data at Mt. Tai.

We confirmed that the FR and NMINP were calculated based on 10-25 nm particles in all cases in this figure.

7. If a p-value appears in a figure or in the paper, then the statistical test needs to be

discussed. What are the null and alternative hypothesis. And why is each hypothesis test implied by each p value important, scientifically interesting, novel, or useful?

Response: The significance of P value will be added in revision.

8. If a regression equation (e.g., y=12.5x+5.6) appears in a figure or in the paper, then its use – either for scientific or engineering purposes – needs to be discussed. The paper has 9 regression equations in it. Are they of any use?

Response: Yes, the equation has its implication. For example, in type A, the Dpgmax and GR can be fitted by the equation: y=12.5x+5.6, with moderate good Pearson correlation coefficient. Based on the obtained equation, newly formed particles could grow beyond 50 nm only when the GR exceeded 3.55 nm h-1 in this type of NPF events. These will be added in revision.

9. I believe all r values can be deleted from the paper without any loss.

Response: Correlation coefficient is a statistical concept, which helps in establishing a relation between predicted and actual values obtained in a statistical experiment. The calculated value of the correlation coefficient explains the exactness between the predicted and actual values. The r values are used to measure the degree of correlation between two variables. A high r value (close to 1) means that the variables are highly correlated, and the fitted equation has its physical meaning. A small r value (close to 0) means the two variables are irrelevant, and the fitted equation is meaningless.

10. Is the size range covered sufficient for calculating the condensational sink? Or stated differently, how much of the condensational sink is being missed by focusing on 10 to 150 or 250 nm.

Response: We recalculated CS based on 10 nm-2.5 μm, 10 nm-300 nm and 10 nm-150 nm particles in 2018. The CS was 0.80$\pm$0.37$\times$10-2 s-1, 0.75$\pm$0.34$\times$10-2 s-1, 0.40$\pm$0.15$\times$10-2 s-1 for the three ranges of particles. In our manuscript, CS was calculated in the range of 10 nm-300 nm, which account for about 94% of particles less

than 2.5 μm. We believe that this size range is sufficient to calculate the condensational sink.

11. Line 138 “can be calculated” or was calculated?

Response: It should be “was calculated”.

12. Are variables that are sensitive to the upper size limit (CCN concentrations that are based on the number of particles greater than size X, condensation sink) consistent given the change in the upper size limit shown in Figure S3, from campaign to campaign.

Response: The upper limit of the size is uniformly 300 nm in 2009-2018. In 2007, the upper limit of the size is 153 nm. The Dpgmax varied from 33 nm to 90 nm in 2007, and didn't affected by upper limit. But the CCN concentrations may be underestimated in some cases due to lack of data in >153 nm particles. For example, figure R7 showed the PNSD on April 23, 2007 when we calculated ΔNCCN. The lognormal fitted curve showed about 15% of the area is missing. Thus, the ΔNCCN might be underestimated in 2007. It will be clarified in revision. However, this will not affect our conclusion that net CCN production largely decreased in 2017–2018.

13. Line 282 – climate change typically requires 30-y averaging. Interannual variability may be much more likely at the time scales studied here.

Response: correct.

14. Line 293 – “data size was small” is vague. A more detailed description of what aspects of the dataset are too small is needed. Response: It will revised to “the data were obtain in seven independent campaigns, each lasted in 18$\sim$70 days, and the data size was small”.

15. Line 294 – there are two issues: spatial representativeness, and sparsity of the record in time. In my opinion these create two different problems for the work. “the data size was small, and we should be cautious in extending the conclusion to a large

spatiotemporal scale"

Response: It will be revised to "1) the data were obtain in seven independent campaigns, each lasted in 20∼70 days, and the data size was small, and 2) the observation was conduct in situ, and it should be cautious in extending the conclusion to a large spatiotemporal scale".

16. Line 299 – this shows the authors are thinking of these events as perfect Lagrangian experiments, where sampling at the mountain site is equivalent to sampling along a 0-D Lagrangian air mass trajectory. Vertical and horizontal mixing are not accounted for in this conceptual model. And the possibility that back trajectories evolve over the course of the PFGE is neglected. In reality, as the event evolves, winds will bring air with a variety of histories (chemical, emissions, radiation, accumulation mode particles, interaction with precipitation and clouds, etc.). The survival probabilities over 100% (Figure 4) are likely a symptom of the fact that reality has complex flows and spatial heterogeneity and does not fit the idealized box model concept.

Response: We agree that the vertical and horizontal mixing play an important role in the observed NPF events. If the ambient nucleation occurs aloft and newly formed particles mixes down to the height to be observed, the observed FR may be determined mainly by the downward moving rate of newly formed particles rather than the true formation rate of newly formed particles. Thus, we change "formation rate" to "apparent formation rate" in revision.

However, the growth rate and Dpgmax of newly formed particles were determined by concentrations and cumulative amounts of the condensed vapors, respectively. The condensed vapors are commonly believed to be generated from chemical reactions in air masses regardless of the moving rates of air masses in vertical and horizontal directions.

It does not make sense to calculate the SP beyond 100% because of highly spatial-heterogeneity of NPF in those particular events. In the revision, we added "Note that

the observed number concentrations of newly grown particles with a larger size sometimes exceeded those with a smaller size under the condition of spatial heterogeneity of NPF. In these cases, SP was not calculated."

17. Figure 7 is of low resolution. Difficult to see some of the symbols, and symbols are of different sizes in different plots.

Response: corrected.

18. The discussions of biogenic and total VOCs throughout the paper are problematic. What species are these? How were they measured? Were the measurements collocated with the PFGE measurements and matched in time? The amount of oxidation needed to grow from 3 to 10 nm or 10 to 20 nm, is quite small, so making broad generalizations about seginficant changes in entire classes of VOCs or in specific compounds, and then connecting them to PFGE is not scientifically valid.

Response: The total VOCs in the June 2006 campaign was cited from Mao et al. (2009), since no data from the spring 2007 campaign were available. As many as 52 VOCs (C4–C12) were measured. The analyses method and the species list can be found in Mao et al. (2009). The total VOCs in the spring 2018 campaign were measured at the laboratory of the University of California at Irvine (UCI), and a total of 78 C2–C10 non-methane hydrocarbons (NMHCs) were measured. We acknowledge that the analyses methods were different in the two campaigns, and we will remove the discussion of VOC data in revision.

19. Rather than making the data available "on request", the data should be publicly posted in machine readable formats at the time of publication in order to allow replication.

Response: Thanks, we will provide the website to access the raw data in revision.

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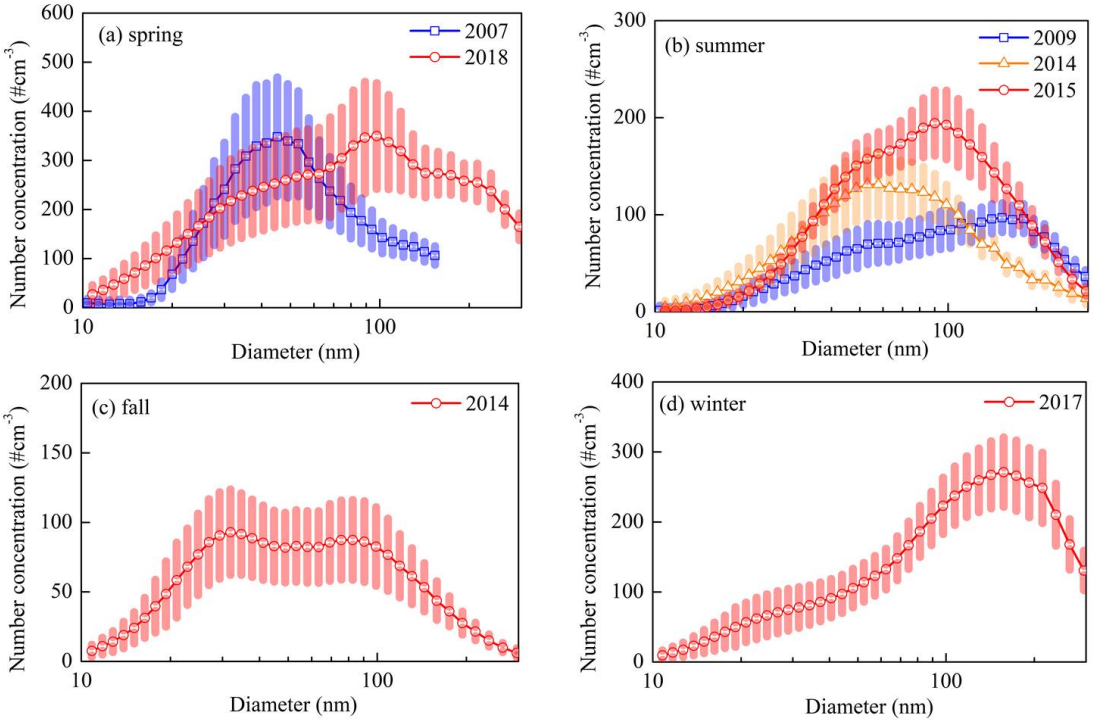

Fig. 1. Figure R1 Particle number size distribution on non-NPF days in each campaign (shaded areas are quarter of the standard deviations).

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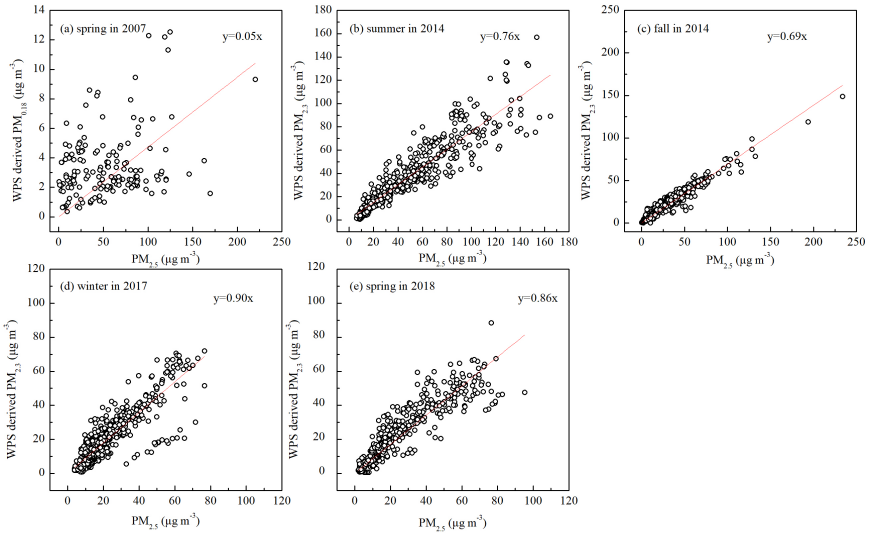

Fig. 2. Figure R2 The relationship between the PM2.5 mass concentration reported by TEOM 1400a or Thermo 5030 SHARP (x-axis) and the PM mass concentration derived from WPS (y-axis).

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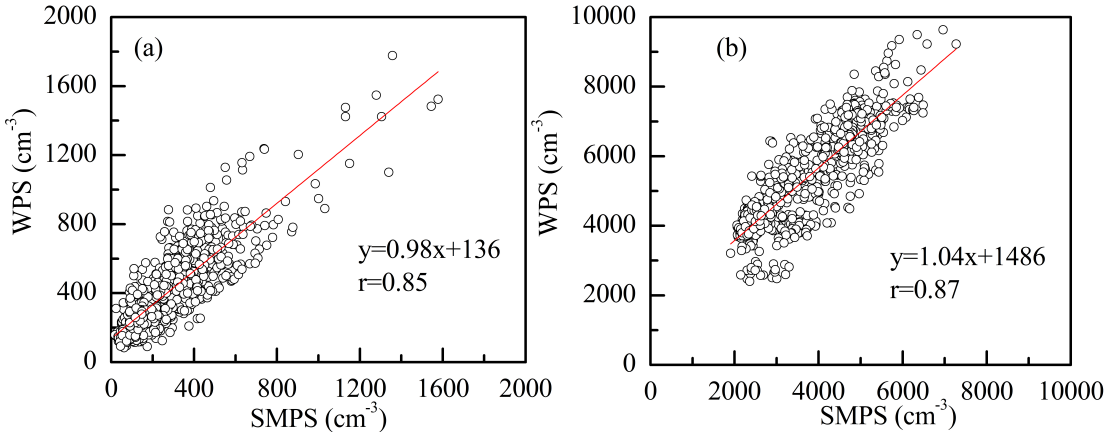

Fig. 3. Figure R3 Comparison of particle number concentration in 10-25 nm (a) and 10-300 nm (b) between WPS and SMPS during 2-7 July 2020.

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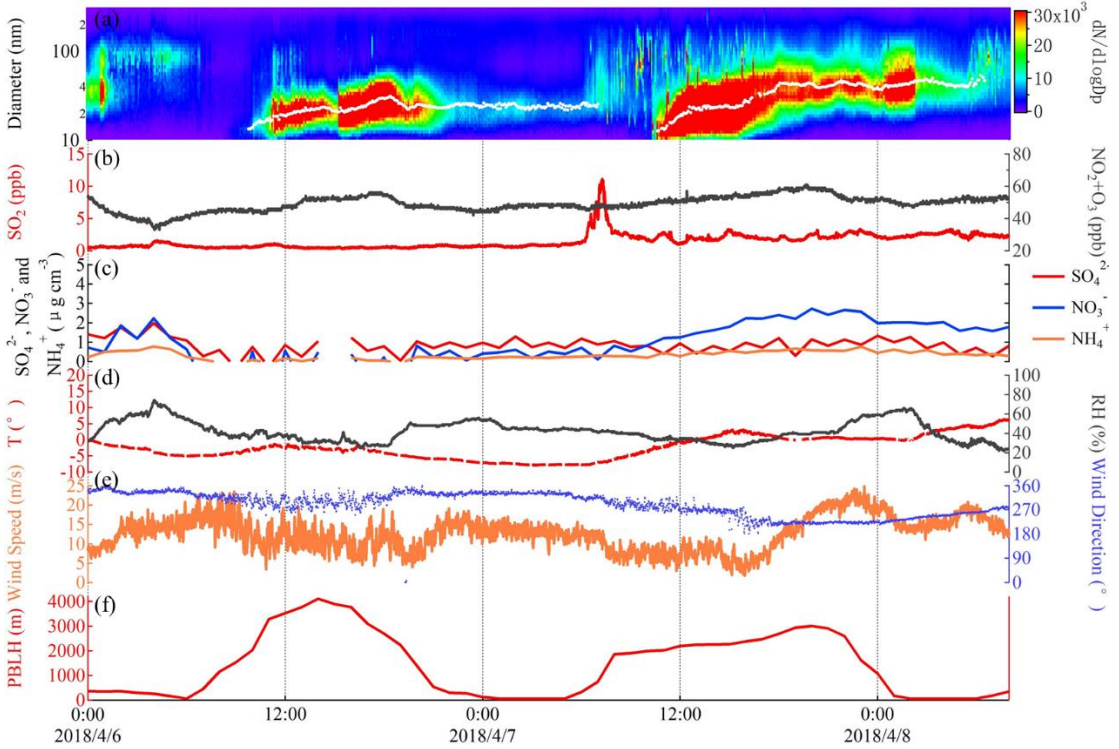

Fig. 4. Figure R4 Time series of NPF events on 6 April 2018 and 7 April 2018: (a) contour plot of particle number size distribution using WPS data; (b) SO2 and NO2+O3; (c) mass concentration of SO42-, NO3- an

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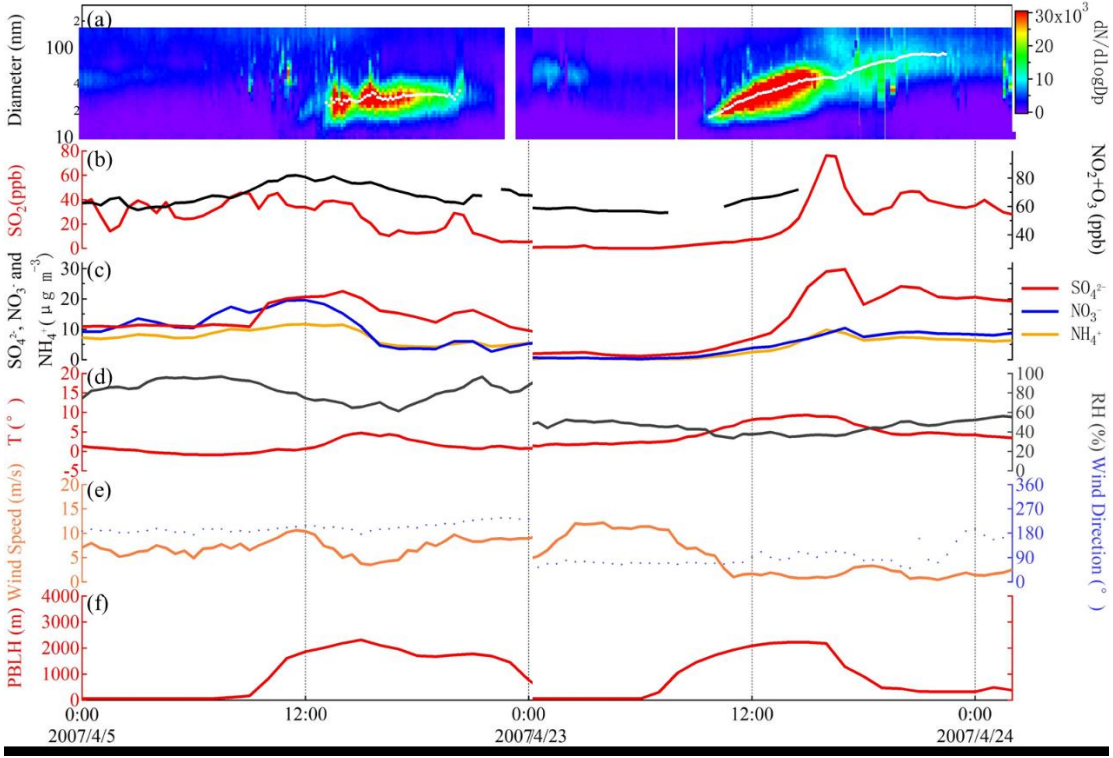

Fig. 5. Figure R5 Time series of NPF events on 5 April 2007 and 23 April 2007: (a) contour plot of particle number size distribution using WPS data; (b) SO2 and NO2+O3; (c) mass concentration of SO42-, NO3- a

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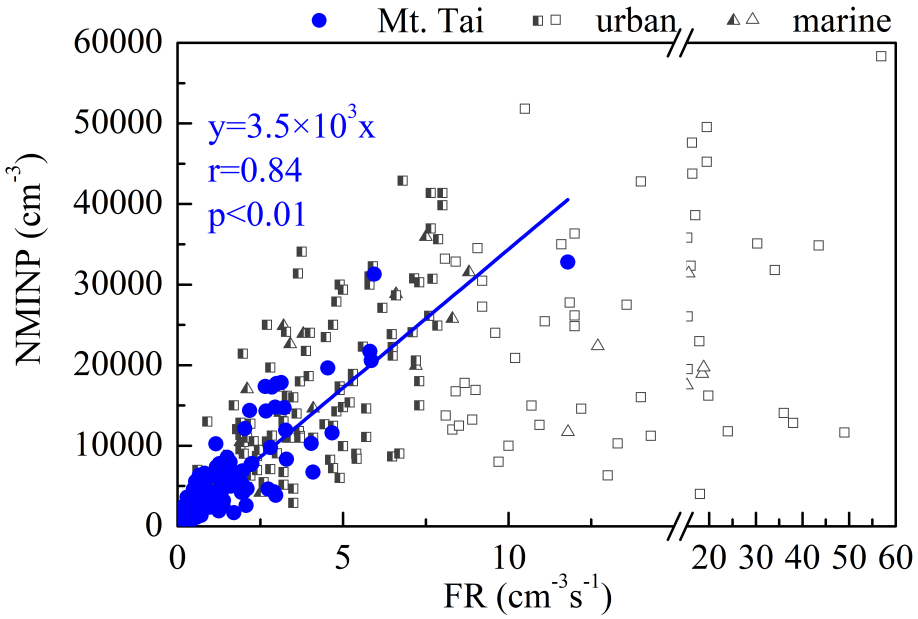

Fig. 6. Figure R6 Relationship between the FR and NMINP in 106 cases of NPF events at Mt. Tai in this study and in urban and marine atmospheres in previous studies (Man et al., 2015; Zhu et al., 2017, 2019; M

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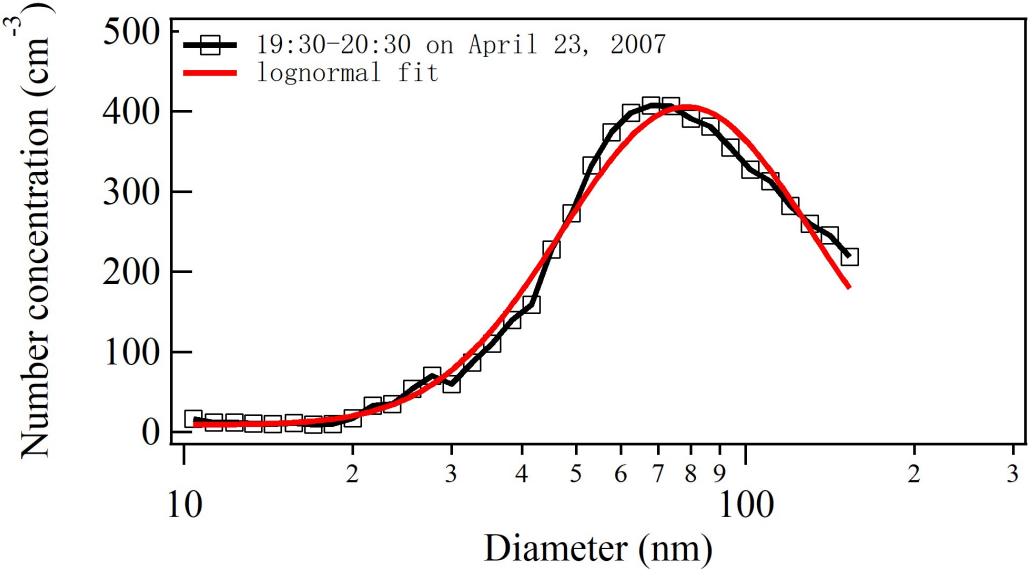

Fig. 7. Figure R7 PNSD during 19:30-20:30 on April 23, 2007, when we calculated ΔNCCN.

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