Response to comments

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)
Thank you for the detailed consideration of the reviewer comments from the first set of reviews at ACPD. I appreciate the checks of key data against independent instruments. I believe this article should be published after minor revisions as outlined below.

Response: The authors appreciate the comments to improve the quality of this study. We will try our best to respond the comments and revise our manuscript accordingly.

Major issues

1. The discussion of increased biogenic VOC and increased HOM, due to afforestataion, as the reason for the observed changes in the apparent formation rate of 10 nm particles is speculative. It should be labeled as a hypothesis. Currently, it is written as if it is a conclusion. It is prominent in the abstract, and in the conclusions. There are qualifications in the paper, but they are not given the prominent placement and strong language that the "conclusion" that BVOC and HOM due to afforestation are a causative agent to the features seen in the manuscript. The BVOC/HOM hypothesis, and its tie to afforestation, should be confined to the discussion and clearly labeled as a hypothesis supported by some suggestive evidence. The evidence presented is insufficient to support it as a firm conclusion.

Response: We agree that no direct observations on long-term trends in BVOC/HOM can be provided to support our analysis at present. We thereby tone down the point throughout the manuscript in the revised version.

The technologies to determine HOM are commercially available recently, therefore, it is practically impossible to gain the data of HOM ten years ago. In addition, BVOCs are highly reactive and have a short life time in ambient air. Therefore, the observed concentration of BVOC always reflects a highly localized feature. On the other hand, NPF events occur in a regional scale. To gain long-term trends in BVOC across regional areas is extremely difficult. To best of our knowledge, no direct observational studies on the trends have been reported in the literature. Thus, our analysis from the rapid afforestation in the literature and those satellite data of leaf area index (LAI) should be given a credit.

2. The language around the increase in VOC overplays the scientific strength of the underlying data. "large increase" (line 20), "rapid afforestation" (line 21), biogenic emissions "changing significantly" (line 75), "rapid increase in BVOCs and their oxidized products as nucleating precursors" (line 94), "difference was highly consistent with the large increase in forest area" (line 365). The authors think it very important that we believe this is a large, rapid, and statistically significant phenomenon. This requires data, not words. The actual data this is based on is much more modest than the language used to describe the VOC changes – and is not actually quantitatively stated in the paper. The percentage increase in springtime BVOC emissions due to

land use change is never stated in the paper. It is difficult to determine from the cited works too (discussed below).

The evidence is limited to the land use map (figure S2) where the increase in tree cover is substantial but not overwhelming, and not consistent in all directions. There are the canister measurements (see comment 3). And there are citations; but actually reading Ma et al. (2019), it is difficult to tell how much the BVOC increase was relative to baseline, where it is happening, and during what seasons it is important. Ma et al. is focused on attributing ozone concentrations during a heat wave to BVOC emission changes that are the result of a heat wave, urban forestry, and land use change. The ozone changes are extensively discussed, the relative change in VOC emissions due to land use change are much less discussed. The delta emissions are mapped in Ma et al. (2019), and appear to be minimal at the location of Mt. Tai. Wang et al. (2020) is also not that supportive. The map shows the delta of carbon fluxes most concentrated well to the south of Mt. Tai, and the time series of above ground biomass increases from 40 to about 43 over about 20 years, or about 0.3% increase per year. A large carbon sink, but not support for "rapid increase in BVOCs and their oxidized products as nucleating precursors." Finally, in the introduction to Ma et al. (2019), another work is cited with increase due to climate change and land cover change may be 1-1.5% per year. This is substantial, and over 11 years could lead to a ~15% change in average regional emissions – I think to claim this is "large and rapid" is stretching and distracts from the strength of the paper, which is the data itself, and the careful calculation of the nucleation and growth parameters.

Response: The arguments on the rapid or large increase in BVOCs and their oxidized products are indeed speculated and should be toned down. We thereby delete the type of words in the revision. However, the increase in afforestation is indeed rapid in China as reported by Chen et al. (2019), i.e., a net increase of ~18% in leaf area from 2000 to 2017. More important, they reported that the leaves green percentage in China is much large than that in developed countries and potentially emit more VOC. The BVOC emissions in China are also simulated to increase over the past decades using the MEGAN model (Zhang, et al., 2016; Chen et al., 2017). The references have been added in the revision.

3. The difference in VOC concentrations between June 2006 (7.0 ± 5.7 ppb) and spring 2018 (16.1 ± 6.5 ppb) is weak and needs further discussion, probably in a supplement – or possibly removal. It is apparently by different research groups, with methods that are not only briefly presented to the reviewers. The time of day of sampling, sampling strategy, and specific compounds are not mentioned and could easily explain the difference. These need to be analyzed properly as an honest species-by-species comparative analysis to tell if there are statistically different concentrations of individual matched biogenic and anthropogenic VOCs – or it needs to be removed. Verification is needed that the samples are appropriately paired (location, time of day, air quality meteorology, season). Taking summer data for comparison to spring data is problematic. In its current form, the discussion of the VOC results seems like data cherry picked to support the predetermined conclusion of an increase in biogenic nucleation precursors, rather than an true hypothesis test.

Response: The sampling methods and analysis of VOCs have added in the supplementary in Test S4, which reads as "VOCs in the spring campaign of 2007 at Mt. Tai were not measured. Mao et al.

(2009) measured the total VOCs at the same sampling site in June 2006, which were used for discussion. Mao et al. (2009) reported the measurements of 52 VOCs (C_4–C_{12}). The details on the method and the species of VOCs can be found therein. Theoretically, the temperature effect should increase BVOC emission more in June than those in spring. In the spring campaign of 2018, a total of 30 whole-air samples were collected for nine days. The collected VOCs were determined by gas chromatography (GC) separation, followed by flame ionization detection (FID), mass spectrometry detection (MSD), and electron capture detection (ECD) at a laboratory of the University of California at Irvine (UCI). 75 VOCs (C_2–C_{10}) non-methane hydrocarbons (NMHCs) were analyzed chemically. The analysis method of samples in 2018 has been reported by Chen et al. (2020). Note that a discrepancy on the measured VOCs between the two labs may exist and cause the uncertainty on the comparison to some extent."

Comment followed by questions 4-7: The exclusion of 3 channels of the SMPS for 30% of hours during the final two campaigns is a big change. I note that it decreased the condensational sink in 2018 by a factor of two. Leaving aside how such a prominent feature could escape the initial QA/QC of the team, the fact that there is now verified instrument error in the 2017 and 2018 campaigns creates an additional requirement for clarity and transparency in the handling of the data. Unfortunately, without knowing more about the root cause for the spurious intermittent counts, it is difficult to trust the remaining 2017 and 2018 dataset. I feel this is important because the 100-300 nm section of the size distribution has a substantial portion of the condensational sink. I note there is what may be a specious peak at 100 nm in Figure S4, which corresponds to the prominent peak at 100 nm in figure S8 and S9 for most of the 2017 and 2018 data. I also note that the PM2.5 vs. WPS reconstructed PM2.5 relationship degrades over time from its best case performance in 2015. The argument that we have increased nucleation rates, lack of growth of nuclei to CCN sizes, an increase in condensational sink, a substantial increase in the size distribution function at 100-300 nm, and a large decrease in PM2.5 mass – this combination is difficult to explain, even by a large increase in HOM that that fuel nucleation but not substantial growth. In my opinion, it requires a source of 100-300 nm particles – either from changes in primary emissions in the region, changes in air pollution meteorology, or instrument error. The authors argue that the time periods are climatologically representative, so that leaves only changes in primary emissions, or instrument error.

Response: The intermittent count error indeed missed from our screening because of three factors: 1) the instrument itself showed that it operated properly; 2) the error is small relative to the total number concentration; 3) it is our expectation for increased number concentrations in 80-300 nm occurring concurrently with decreasing mass concentrations of $PM_{2.5}$, based on our unpublished independent measurements made in a coastal megacity of China using a fast mobility particle sizer over the last decade. The third factor is out of the scope of this study, and don't detail here.

Figure R1 showed an example when ~100 nm particles prominent in an NPF day at Mt. Tai. In Figure S9, the prominent peak at ~100 nm appeared in 2009, 2014, 2015, 2017 and 2018. We also examined the relationship between SO_2 and the particle population between 100-300 nm ($N_{100\text{-}300nm}$). As shown in Figure R2, SO_2 and $N_{100\text{-}300nm}$ exhibited the moderate linear relationship in each campaign, although the slope varied on campaigns.

We thank the reviewer very much help us to find the instrument error around 213 nm, which

also reminds us to be more careful. It also indicates that the peer-review process is so important to correct the type of errors. Actually, most of the data in 2017 and 2018 didn't suffer from the problem. We will contact with instrument vendor to check what exactly took place.

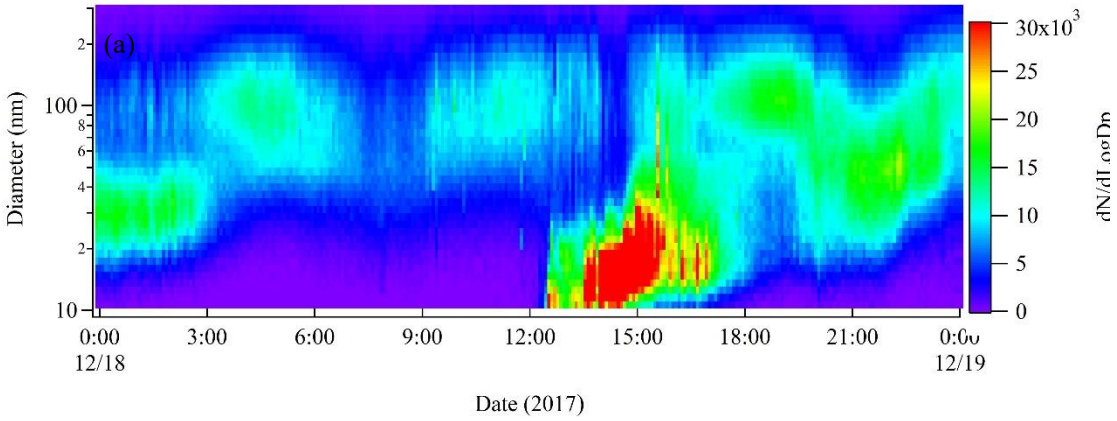

Figure R1 Contour plot of the particle size distributions on NPF days on 18 Dec. 2017.

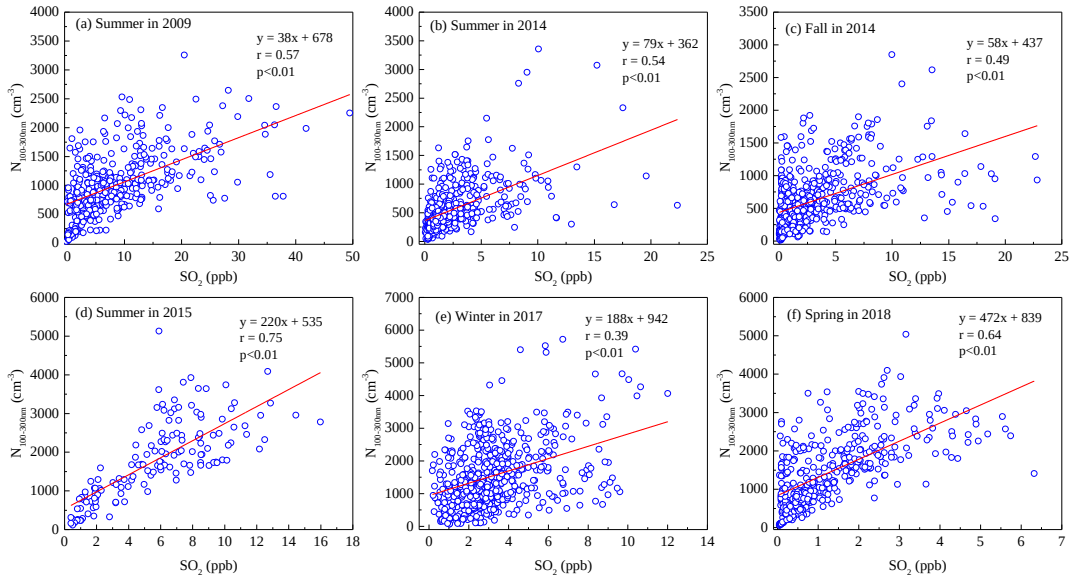

Figure R2 The relationship between SO_2 and particle number concentration in 100-300 nm ($N_{100-300nm}$).

Specific questions related to this:

4. Was exclusion of three channels around 213 nm enough? Were all the needed times excluded? What was the test used to determine if a period was to have those channels excluded?

Response: We checked the WPS data in 2017 and 2018. The errors around 213 nm occurred only in approximately 30% of the sampling days and correct accordingly. The errors are almost constant. After knowing the error, it is easy to be excluded.

An example with instrument error on an NPF day (27 Mar. 2018, contour plot in Fig. S4b) was shown in Figure R3. Particle number concentration in three bins of 192 nm, 213 nm and 237 nm

were abnormally high. Thus, the three bins were excluded in the statistical analysis (e.g., the calculation in Fig. S5, S8, S9). For the calculated CS, the error data were smoothed interpolated from 173 nm to 294 nm as shown by the purple dots and lines. This has been added in the revised Figure S4.

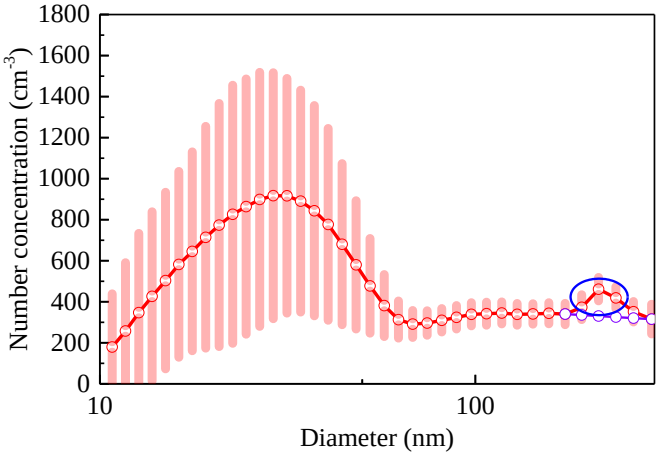

Figure R3 Particle number size distribution on 27 Mar. 2018 (shaded areas are the standard deviations, three bins inside blue circle were exclude from analysis, purple dots are smoothed interpolated data from 173 nm to 294 nm).

5. How is the QA/QC and the replacement of data with smoothed interpolated data marked in the files that are now publicly available? This needs to be clearly explained in the supporting data files.

Response: Sure. It has been added in the revised Figure S4 because the same problem may also occur in previous studies in the literature or future studies in research community.

6. Show, in addition to the number count vs. number count comparison of instruments (Figure S3), the size distributions functions for hours where both instruments ran collocated. Comparing the number counts rather than the size distributions can hide substantial problems. Do the size distributions match, or does the WPS have some extra peaks? This would be a strong indication of the quality of the size distributions shown in Figures S8 and S9, and the condensational sinks and other parameters calculated from them. The size distributions should be shown with no data removal, and then with the removal/smoothing of suspect malfunction channels/peaks.

Response: The comparison of particle number size distribution between WPS and SMPS was shown in Figure R4 (also added in revised supplementary materials). Both instruments showed unimodal distribution when no NPF events occurred during the instrument comparison. There was small difference in the peak of the particle mode, i.e., 56 nm for WPS and 64 nm for SMPS, which may be due to either the system difference between them or ~1.5 km distance between them. No data were removal in Figure R4, which has added in the caption. However, that the error of 213 nm particles was eliminated.

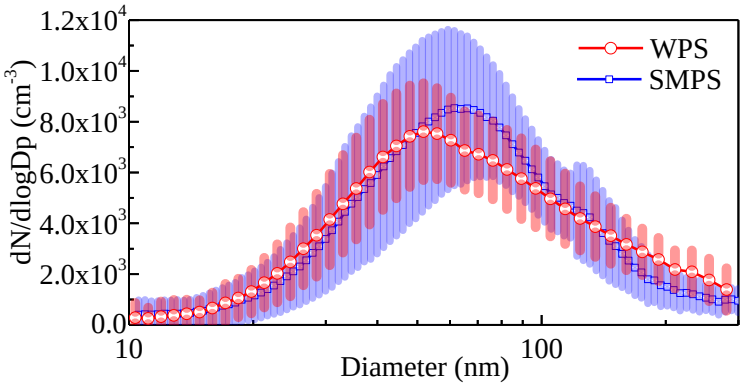

Figure R4 Particle number size distribution between WPS and SMPS during the summer campaign in 2020 (shaded areas are the standard deviations).

7. The secondary peak at 100 nm in Figure S12 is quite striking. With a height of dN/dlogDp at 15,000 cm-3, and nearby minima at 5,000 cm-3 at 30 nm and at 250 nm, it really is a very sharp feature. Given problems at 213 nm, what checks were made to make sure this peak is real? The feature in Figure S12 is correlated with the PFGE, but abruptly disappears when instrument trouble strikes at 18:30, as indicated by the blue lines at 213 nm. There is also a faint indication of a "band" at 100 nm in Figure S4 for some 2018 data (and the data in question has acknowledged problems at 213 nm) – and it is appreciable in size, reaching dN/dlogDp at 10,000 cm-3. Such sister peaks appear in some PFGE datasets due to collocated sources of nucleation precursors with Aitken/accumulation mode particles; but such sister peaks seem (at least on average) absent from the Mt. Tai data prior to about 2017. For example, such a sister peak at 100 nm is totally absent in the 2014 figure shown (S12e).

My questions: after Figure S12 (or Figure S4) has gone through the exclusion process for the 213 nm 3-channel problem, is all the remaining data considered valid? What checks were made to make sure this 100 nm peak, growing in prominence in 2017 and 2018 (the same time as the 213 nm problem appears), is real? Do the other continuous instruments (for figure S12) support the existence of the 100 nm feature prior to 18:30. If from a primary source for the 100 nm mode, there is often correlation with PM2.5, CO2, EC, NOx, CO, and/or SO2. Is there an abrupt air mass change for S12 at 18:30 needed to support disappearance of virtually all particles? Presumably this is change from upslope (polluted) air to free tropospheric air. But now with the instrumental problems appearing in 2017 and 2018 – every opportunity to show instruments working properly and reporting valid data should be taken advantage of.

Response: As shown in Figure R5, particles with the peak around 100 nm was associated with the low wind speed (<2m/s) and increased concentration of gaseous air pollutants, i.e., SO_2 and NOx (11:30-18:30). It seems that the increased number concentration of ~100 nm mode particles was due to the accumulation of air pollutants. The particle mode jumped to around 200 nm after 19:00, when the wind speed increased to ~6m/s. Meanwhile, the secondary chemical components, i.e., SO_4^{2-}, NO_3^- and NH_4^+ in $PM_{2.5}$ largely increased by a factor of 5~6. This indicated that heterogeneous reactions may occur and lead the particles grow to the larger sizes. However, the 213 nm bins suffered the error, and the increased particle mass concentration cannot be accurately quantified.

Combined with Figure R1 and R2, we confirm that the particle mode around 100 nm was the true

signal, and they moderately correlated with SO_2 concentration. The increase of ~100 nm mode particles was due to either the long-range transport of air pollutants, or accumulation of air pollutants under low wind speeds.

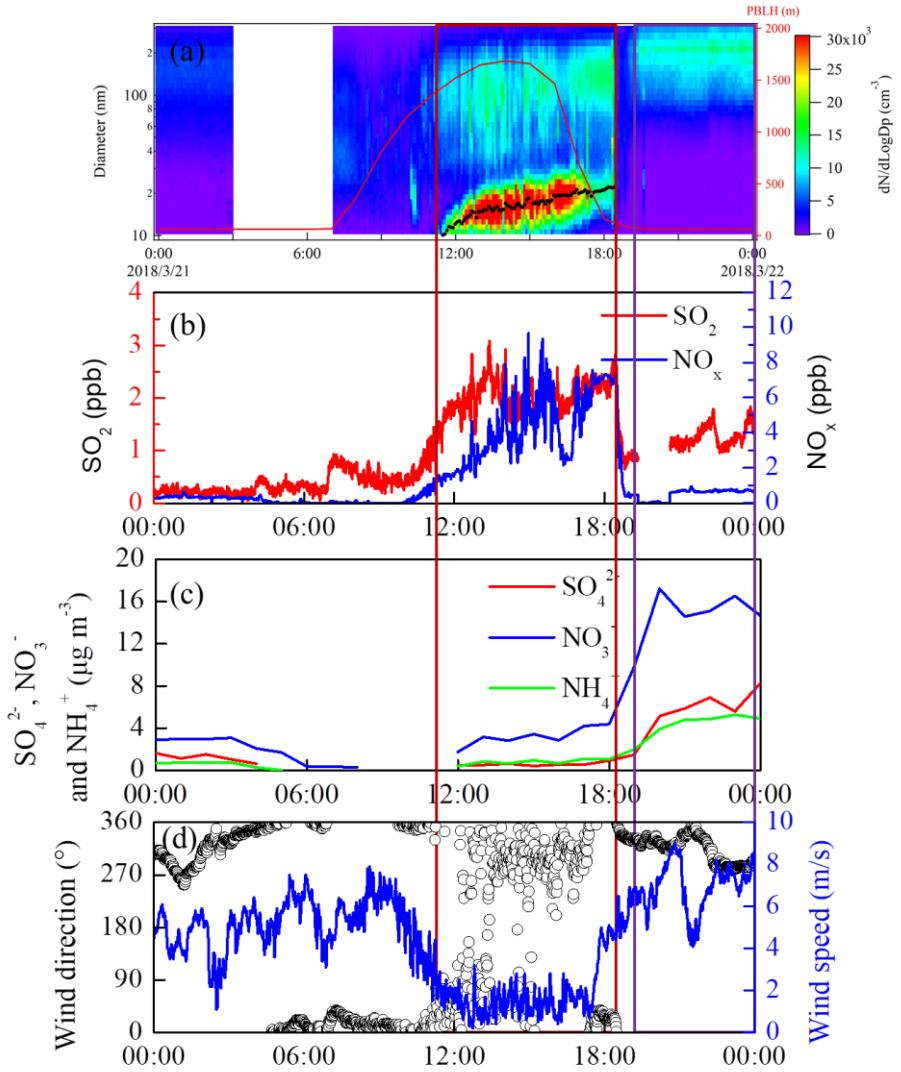

Figure R5 Contour plot of NPF event, planetary boundary layer height (PBLH), time series of gaseous SO_2, NOx and particular SO_4^{2-}, NO_3^- and NH_4^+, and wind direction and wind speed on 21 Mar. 2018.

Minor issues

8. Figure S12 seems to be prior to the data manipulation around 213 nm.

Response: Yes, we didn't modify the contour plots on this issue.

9. Figures S8 and S9 should have y axis as dN/dlogDp so that they can be more easily compared to the other figures in the paper that use dN/dlogDp and to other publications. Using dN as the y axis makes the height dependent on the bin spacing.

Response: Corrected.

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