Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-1064-AC3, 2021

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Enhancement of nanoparticle formation and growth during the COVID-19 lockdown period in urban Beijing" *by* Xiaojing Shen et al.

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Received and published: 20 February 2021

In this study, the authors compare observations before, during and after the lockdown period in China during January and February 2020. They observe an enhancement of the nucleation and growth process of nanoparticles during the lockdown in Beijing. From this, they conclude that these findings were caused by the lockdown period, mainly due to lower concentration of Aitken mode aerosols that reduces the condensation sink. In contrast, accumulation mode particles increased and caused pollution events, due to new particle formation events with subsequent growth. This enhanced particle nucleation and growth is attributed to enhanced values of H2SO4 and VOC ox-

idation products, which were calculated from available data. The subject of this study is certainly suited for ACP. However, I have two major concerns regarding this study that need to be addressed in a revised version. These concerns are a) meteorological representativeness and b) statistical significance. I explain my concerns in detail in the following.

Response: The authors thank the reviewer's comments and try our best to address the issues point-by point.

Major issues: a) Meteorological representativeness A major problem when comparing air pollution data from different periods is the influence of meteorology. This needs to be considered to ensure that the observed differences are not coincidence. High and low pressure systems may prevail for a certain time, leading to differences in cloud coverage and thereby to enhanced or reduced radiation. Wind speed and direction influences transport of pollution from sources, either regional or even from long distances. Meteorological parameters are available. I suggest conducting something like a 5-year climatology of the available parameters to check the variability of the atmosphere and the representativeness of the Jan-Feb 2020 period, especially the lockdown period, compared to the same period in previous years. In line 40-41, the authors state that "Furthermore, particle accumulation was favored by stagnant airflow and vertical meteorological conditions during LCD (Zhong et al., 2020)." So apparently, they are aware of unusual meteorological conditions during the LCD period. But, since the Zhong et al. reference is still in preparation, the reader can't retrieve this additional but important information.

Response: Thanks for the reviewer's constructive comment. (1) The meteorological parameters during LCD period, January and February in 2020, as well as the average conditions of January and February in 2016-2020 were analyzed and the diurnal patten was given (Fig. 1). It showed much higher RH, lower wind speed, slightly higher temperature and lower pressure during LCD and January and February 2020, than that of 5-year climatology average condition (January and February in 2016-2020).

The anomaly of monthly mean sea level pressure in January and February between 2020 and 2016-2020 was analyzed based on the ECMWF reanalysis dataset (ERA5, https://cds.climate.copernicus.eu/), as given in Fig. 2. It showed negative anomaly in Beijing-Tianjin-Hebei Province, indicating the air pressure decreased in January and February in 2020, as compared with the corresponding period of the 5-year climatology. The local air convergence resulted in high RH and low wind speed, which favored for the air pollutants accumulating. (2) In line 40-41, we removed the Zhong et al., 2020 in the manuscript and referred the previous publication (Zhong et al., 2018) also conducted in Beijing to address the meteorological effect on the air pollution formation. The discussion was supplemented in the section of “3.1 The meteorological conditions”.

b) Statistic significance The changes in NPF event frequency seem not to be significant, because the number of NPF events is small. The authors report on differences of "10 out of 23 days (43%)", "8 out of 24 days (33%)", and "5 out of 13 days (38%)". These are small numbers. A simple estimation based on Poisson statistics suggests that these differences may not be significant. Here a detailed statistical analysis has to be presented, and it may be that the results will be that these differences are not significant. Similar analyses have to be done for pollutants NO2 and SO2, because Fig. 3 shows that both are highly variable during the pre-LCD, LCD, and post-LCD periods. The linear regressions between H2SO4, J2, and GR are significant (Fig 5), but that’s not new. And since H2SO4 is mainly calculated from global radiation, the meteorological influence on this parameter is high. The different growth rates when comparing pre-LCD, LCD and post-LCD for the different size ranges presented in Fig 6 may also not be significant, regarding the error bars.

Response: (1) The Poisson statistics was conducted for NPF event occurrence probability for pre-LCD, LCD and post-LCD period, respectively, as given in Fig. 3. It showed almost the same NPF event occurrence probability as compared with pre-LCD and LCD period, but fewer NPF event during Post_LCD. (2) The probability density function (PDF) was given for SO2, NO2 and O3 during Pre_LCD, LCD and Post_LCD, respec-

tively, as given in Fig. 4. It showed significant decreasing trend of NO2, whereas increasing trend of O3 as compared with Pre_LCD and LCD/Post_LCD. However, the variation of SO2 among different periods was not clear, as the SO2 concentration remained low due to the emission control these years. The PDF of gases pollutants and the detailed discussion have been added in the text and the figure is given in the supplementary materials. (3) H2SO4 proxy was derived by three methods and the average value was applied for discussion, in order to minimize the uncertainties. (4) the growth rate (GR) was discussed for different size range 2-5 nm, 5-10 nm and >10 nm, respectively. It showed GR2-5nm and GR>10nm were generally higher during LCD/Post_LCD as compared with Pre_LCD, however, the difference of GR5-10 nm is not clear.

Minor comments

1. Line 20: Please explain the meaning of J2 also in the Abstract.

Response: It has been revised to be “higher formation rate of 2 nm particles (J2) and the subsequent growth rate (GR)”.

2. Line 34-35: Reformulate this sentence to: The number of Aitken mode particles (d$\sim$ 25 – 100 nm), which is related to traffic emissions (Deventer et al., 2018) is also expected to decrease.

Response: It has been revised in the text.

3. Line 38: Change "Air pollution is driven by the enhancement of secondary particles, “ to "Secondary particles contribute significantly to air pollution“

Response: It has been revised in the text.

4. Line 41: The reference to Zhong et al. in preparation is not sufficient. If you do not want to show these data now, then I suggest to wait until the Zhong et al. paper is submitted as well. The meteorological situation (e.g. the inversion layer) is of great importance (see my major comment above).

Response: we removed the Zhong et al., 2020 in the manuscript and referred the previous publication (Zhong et al., 2018) also conducted in Beijing to address the meteorological effect on the air pollution formation. The discussion was supplemented in the section of "3.1 The meteorological conditions".

Zhong, J., Zhang, X., Dong, Y., Wang, Y., Liu, C., Wang, J., Zhang, Y. and Che, H.: Feedback effects of boundary-layer meteorological factors on cumulative explosive growth of PM2.5 during winter heavy pollution episodes in Beijing from 2013 to 2016, Atmospheric Chemistry and Physics, 18(1): 247-258, DOI: 10.5194/acp-18-247-2018, 2018.

5. Line 107 – 113: H2SO4 estimation: This is a very rough estimation. What are usual values for k, and what is the dimension of k? In Figure 4 no units are given on the right y-axis, but shouldn't that be cm-3?

Response: The concentration of H2SO4 was not measured directly in this study and different proxy methods were referred to derive the proxy sulfuric acid. A method (Eq. 3) depends on the global radiation (Glob_R), SO2 and condensation sink (CS), and is developed according to the previous study conducted in a forest site, Hyytiälä, Finland (Petäjä et al., 2009).

$$[H2\,SO4\,]=(k\times Glob\_R\times SO2)/CS \quad (1)$$

where k is empirically derived factor and well correlated with Glob_R ($k=1.4\times10\text{-}7\times Glob\_R\text{-}0.7$, unit: m2 W-1 s-1). The proxy equation is site-specific due to the different atmospheric conditions. In the polluted atmosphere, such as in Beijing, several proxy methods were also constructed based on a number of available atmospheric parameters (Lu et al., 2019). In this study, the simplest proxy (Eq. 4) and best performance proxy (Eq. 5) are adopted to derive the proxy sulfuric acid.

$$[H2SO4\,]=280.05\times UVB\hat{}0.14\times[SO2\,]\hat{}0.40 \quad (2)$$

$$[H2SO4\,]=0.0013\times UVB\hat{}0.13\times[SO2\,]\hat{}0.40\times CS\hat{}(-0.17)\times([O3\,]\hat{}0.44+[NOx\,]\hat{}0.41) \quad (3)$$

[H2SO4] is the gaseous sulfuric acid with the unit of molecule cm-3. [SO2], [O3] and [NOx] is the concentration of sulfur dioxide, ozone, and nitrogen oxides, with the unit of molecule cm-3. UVB is the intensity of ultraviolet radiation b in W m-2. CS is the condensation sink, which describes how fast the vapor molecules condense on the existing particles (Dal Maso et al., 2002), with the unit of s-1. The proxy method has been validated by comparing the measured sulfuric acid with a high correlation coefficient of 0.86 (Lu et al., 2019), based on the field campaign conducted approximately 2 km away from CAMS site. In this work, the direct measurement of UVB was not available. However, it had been reported by Hu et al. (2013) that the monthly average of the ratio of UVB to global radiation (Glob_R) ranged from 0.007 to 0.017% in Beijing. And in this study, the average ratio of January and February (0.008%) was applied to derive UVB by $0.008\%\times Glob\_R$.

6. Lines 123-130: So, to infer VOC oxidation capacity, you don't have OH measurements, thus you approximate OH, but you don't have UVB, so you approximate by global radiation. This seems like many uncertainties. Can you comment a little more on the uncertainties and the influence they might have on your interpretation?

Response: As discussed above, the UVB was derived by 0.008% ïĆť Glob_R, based on the previous study that the monthly average of the ratio of UVB to global radiation (Glob_R) ranged from 0.007 to 0.017% in Beijing (Hu et al., 2013). The average ratio of January and Feburary (0.008%) was applied in this study for calculating [H2SO4].

7. Line 126, Equ. 6: There is a ratio of two numbers (8.4e-7/8.6e-10). Are these numbers rate coefficients that should have units? Or are they just empirical fit parameters? If they are just parameters, you can replace them by 9.8e2.

Response: The equation has been removed from the manuscript.

8. Line 132-135: What are the exact criteria to define the NPF events?

Response: It has been revised to "NPF events are identified and different nucleation

types are characterized based on the daily evolution of particle number size distribution (PNSD). The burst of nucleation mode particles with diameter $\leq$ 25 nm appeared in the PNSD, and the burst should prevail over a few hours with clear growth process (Dal Maso et al., 2005)."

9. Line 140-142 & 178: As already commented above: "The NPF event occurred on 10 out of 23 days (43%) during pre-LCD, 8 out of 24 days (33%) in LCD, and 5 out of 13 days (38%) in post-LCD, respectively". The frequencies of 43% or 33% are based on a very low number of events. Please add the total number of events to the table, and calculate Binomial or Poisson statistics for these numbers. It may be that the differences are too small to be significant, just by the small number of events.

Response: We gave the number of NPF days and total available measurement days in table 1, instead of the NPF frequency. The Poisson statistics was conducted for NPF event occurrence probability for pre-LCD, LCD and post-LCD period, respectively, as given in Fig. 1. It showed fewer NPF events with higher probability as compared with pre-LCD and LCD period.

10. Line 150: Please refer to Fig 2a here and replace ". . .were discussed in detail." by "are discussed in detail in the following". Otherwise it is hard for the reader to follow this discussion.

Response: The sentence has been revised to "were given in Fig. 2a and discussed in detail in the following."

11. Line 170/171: Refer to Fig 2b here.

Response: It has been revised in the text.

12. Line 174: Refer to Fig 2c.

Response: It has been revised in the text.

13. Line 180: What is J3? Should it read J2? Or does this refer to measurements from

2015 where 3 nm was the lower size? If so, please explain.

Response: A sentence was given to explain the meaning of J3 in Line 185 "J3 referred the formation rate at 3 nm calculated from the particle number concentration of 3–4-nm particles by Eq. (1), as the lowest detection limit of SMPS applied in 2015 and 2010-2013 campaign was 3 nm."

14. Line 182-184: "in this study", "The previous study". Please make clear which study is which.

Response: "in this study" refers to the results of this manuscript and "the previous study" are the references we cited (Lehtipalo et al., 2018, Yan et al., 2020). The sentences have been revised to be "The daily mean value of NO2 decreased by $\sim$35% and SO2 decreased by $\sim$13%, whereas O3 increased by 80% during LCD as compared to pre-LCD in this work (Fig. 3). Previous studies had indicated that NOx suppressed NPF events by influencing the formation of highly oxygenated organic molecules (HOMs), which participated in nucleation and initial particle growth (Lehtipalo et al., 2018; Yan et al., 2016; 2020)."

15. Line 191: " As discussed separately for LCD and pre-LCD during the NPF event occurrence (9:00–16:00 LT),. . .". Which NPF event are you talking about? You specify the time period 9:00 – 16:00 LT. But Fig. 4 shows a time series of the whole campaign. Individual events can not be seen here. The whole paragraph line 191 until line 200 can not be understood, because you refer to one NPF event that is not shown. Which day is that? I assume that this text describes an event that was discussed in Huang et al 2020, but if that is so, this discussion does not belong here in this paper. Please include a time series of the measured parameters for this event here or skip this paragraph.

Response: "the NPF event occurrence (9:00–16:00 LT)" indicates all the NPF events usually occur during the daytime (9:00-16:00 LT), not refers to a specific NPF event. And the paragraph line 191 until line 200 are the discussion based on Fig. 4, describing the general characteristics of all NPF events during the measurement. We reorganized

this paragraph to make it clearer.

16. Line 201: " : : :was indicated by different VOC_ox,capacity levels" seems not to be the right expression here. I suggest to rephrase the whole sentence: "Both the H2SO4 proxy and the VOX_ox,capacity were correlated to J_2,tot and to GR (Fig 5)."

Response: The sentence has been revised according to reviewer's comment.

17. Line 205-207: This is again a result from another study. Make that clear at the beginning of the sentence, like "Stolzenburg et al. (2020) showed that sulfuric acid could not explain: : :."

Response: the sentence has been revised to "Stolzenburg et al. (2020) revealed that sulfuric acid played an important role in smaller growth processes from 2–10 nm, however, could not explain condensational growth when the nucleated particles overcame 10 nm"

18. Lines 208-210: If H2SO4 contributed more to the nucleation process and organic vapours to the growth, would you not expect to see a better correlation between H2SO4 and J2 than between H2SO4 and GR, and similarly a better correlation between VOC_ox,cap and GR than between VOC_ox,cap and J2?

Response: The proxy sulfuric acid was re-calculated based on the reviewer's comment, and the effect of sulfuric acid on formation rate (J2) and initial growth rate (GR). The influence of H2SO4 on J2 and GR was re-evaluated, and it showed a slightly higher correlation coefficient (R) of J2 (R=0.62) than the GR (R=0.45). However, the oxidation product could not be estimated simply, but also discussed in the manuscript. The estimation of VOCs oxidizing capacity was removed in the manuscript, as the proxy method was not reasonable as the reviewer suggested. However, the direct measurement data of 5 major kinds of VOCs is supplemented and the variation is discussed. The major oxidants of VOCs were also found to be elevated during LCD, indicating the possibility of enhanced oxidation products of VOCs that promoted the nucleation and

growth process.

19. Lines 214-215: For the size range 5-10 nm, there is no significant difference between ions and neutral particles. Especially the yellow bars for 5-10 nm (Fig. 6) have almost exactly the same height. What are the error bars and what is their meaning? This should explained in the caption of Fig 6.

Response: The detailed growth process of the nucleated particles and ions on NPF days was given in Fig. 5. It showed Dp,nuc,ion grow faster than Dp,nuc,par, especially for the sizes below 5 nm, depending on the growth rate in each time interval ((Dp,nuc,t1- Dp,nuc,t2)/Δt, Δt = 1 h). The enhanced growth rate factor (GRp,nuc,ion/ GRp,nuc,par) ranged from 1.1 to 2.0, with the average of 1.38+-0.34. The enhancement was higher in sub-10 nm particles, whereas it decreased as the particles grew to larger sizes. In addition, the histogram and error bars represent the mean value and standard deviation, respectively, which has been clarified in Fig. 6 caption.

20. Line 220: What is the enhancement factor? How is it calculated?

Response: The enhancement effect (EF) describes the dipole-charge interaction on the growth of charged clusters (Nadykto and Yu, 2003). The charge effect of ions on the NPF include accelerated rates of vapor condensation and particle coagulation, as well as the charge recombination (Yu and Turco, 1998; 2000). EF for the pure species participating NPF event (eg, sulfuric acid, VOCs) can be calculated as the below equation (Nadykto and Yu, 2003):

EF=1+(2lE(r_p+r_m)L(lE(r_p+r_m)/kT+$\alpha\varepsilon$_0 Eˆ2 (r_p+r_m)))/3kT (4)

EF depends on temperature (T), size of charged particles (r_p), and microphysical properties (dipole moment: l, polarizability: α, and size: r_m) of vapor molecules. For sulfuric acid molecules, EF could be 10 for ions with $\sim$0.5 nm but decreased quickly to 2 for uptake by a charged particle of $\sim$2 nm, at T=300 K (Nadykto and Yu, 2003). In this work, we used enhancement factor (GRion/GRpar) to denote the net influence of

charge on the particle growth. In order to differentiate with EF defined by equation 4, we used “enhanced growth rate factor” to denote GRion/GRpar. We also re-organized the section “effect of charge ions” to make it easier to understand.

References:

Nadykto, A. B. and Yu, F.: Uptake of neutral polar vapor molecules by charged clusters/particles: Enhancement due to dipole-charge interaction, J. Geophys. Res., 108(D23), DOI: 10.1029/2003jd003664, 2003.

Yu, F. and Turco, R. P.: The formation and evolution of aerosols in stratospheric aircraft plumes: Numerical simulations and comparisons with observations, Journal of Geophysical Research: Atmospheres, 103(D20): 25915-25934, DOI: 10.1029/98jd02453, 1998.

Yu, F. Q. and Turco, R. P.: Ultrafine aerosol formation via ion-mediated nucleation, Geophys. Res. Lett., 27(6): 883-886, DOI: 10.1029/1999gl011151, 2000.

21. Line 223: Replace "effect of the charger" by "effect of charge"

Response: It has been revised in the text.

22. Lines 228-231: It would be helpful to add PM2.5 to one of the time series in Fig. 3, and to add the numbers of the NPF events in Fig 3 and 4 instead of or additional to the crosses. When I count the NPF events marked by the crosses, I find that event #9 is on January 23.

Response: The figures has been revised as in Fig. 6.

23. Lines 233-238: Please include a graph showing PM2.5/CO. Please also state clearly how pollution periods were identified.

Response: The discussion from lines 233-238 are referred to Fig. 7, which have contained PM2.5/CO in subplot (b). We revised the sentence as “Two principal pollution episode formation stages were identified according to variations in the PM2.5 mass

concentration dividing by CO (PM2.5/CO), as indicated in Fig. 7b.”. The pollution episodes were defined as the daily mean value of PM2.5 mass concentration exceeding 75 μg m-3, which is the criterion value of the second grade of air quality in China. We have added this sentence in the text.

24. Line 238-240: This sentence doesn’t make sense. Maybe the "and" before "unfavorable" needs to be deleted?

Response: It has been revised in the text, “and” has been deleted.

25. Whole Section 3.4: What is the message of the section 3.4? The reader can not see the pollution events if there is no graph showing PM2.5, or CO, or both. Are there any conclusion drawn by section 3.4? It all seems very speculative. Meteorological conditions are mentioned as one possible reason for this pollution event, but it is not investigated by trajectory and emission source locations.

Response: The discussion of section 3.4 is referred to Fig. 10, including the evolution of PNSD, PM2.5 and its normalization by CO, which has been clarified in the text. The meteorological factor including wind direction, speed and relative humidity has been given in Fig. 10. Furthermore, the back-trajectory analysis from Feb, 4th-14th, corresponding to the study period in Fig. 10, is also supplemented (given as Fig. 11 in the manuscript). The back trajectories originated from northwest from February 4th to 10th, corresponding to the dry and clean air masses (Fig. 7). However, from February 11th to 13th, the southwesterly air masses were dominated and favored the accumulating of the particles, resulting in the high concentration level of particle matter.

A paragraph of “2.5 Back trajectory analysis” is given in the section of “2. Method” In order to reveal the meteorological condition during the pollution case formation, the 48 h backward trajectories arriving at CAMS stie were calculated at 12:00 Local time, terminating at the height of 500 m above ground level by applying the Trajstat Software, combined with HYSPLIT 4 model (Hybrid Single-Particle Lagrangian Integrated Trajectory) and using the NCEP GDAS (Global Data Assimilation System) data with 1°*1°

resolution (Draxler and Hess, 1998, Wang et al., 2009).

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-1064, 2020.

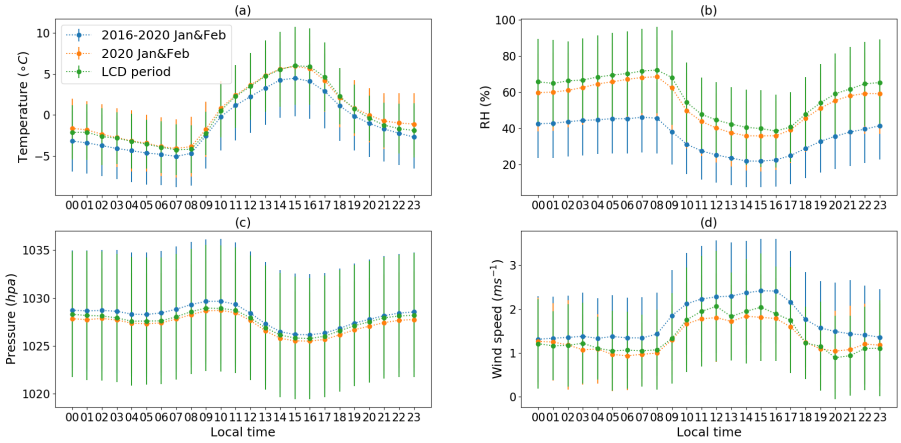

Fig. 1. The mean diurnal pattern of meteorological parameters, including temperature (a), RH (b), sea level pressure (c) and wind speed (d) during LCD period and reference period.

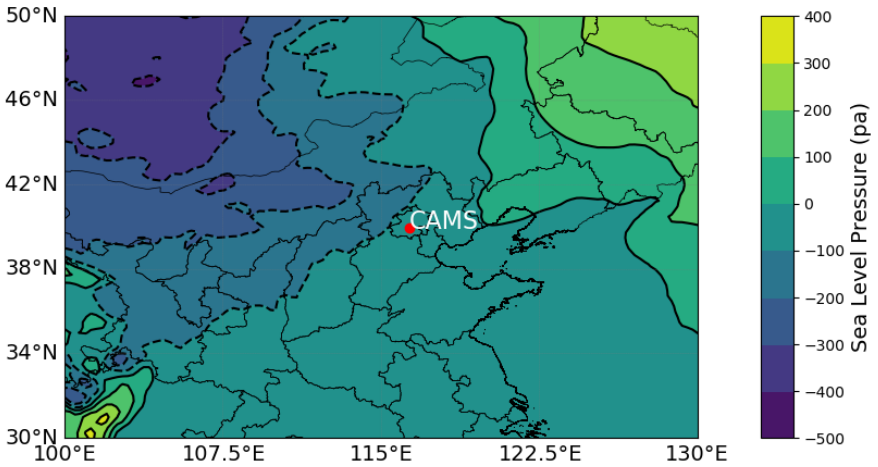

Fig. 2. The anomaly of monthly mean sea level pressure in January and February between 2020 and 2016-2020.

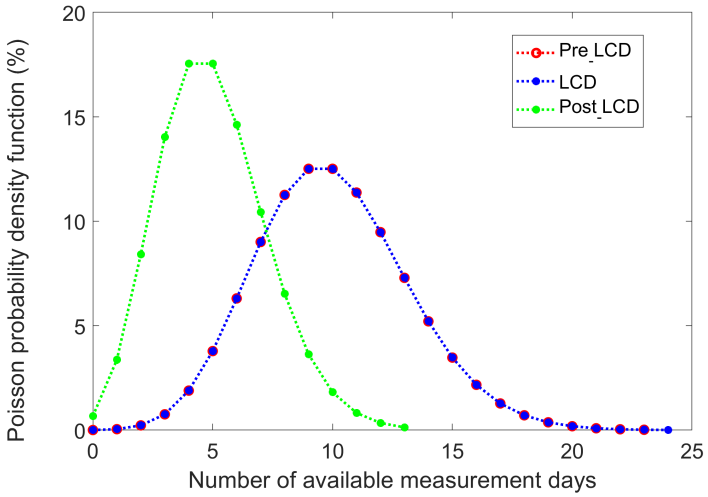

Fig. 3. Poisson distribution of NPF event occurrence frequency during pre-LCD, LCD and post-LCD, respectively.

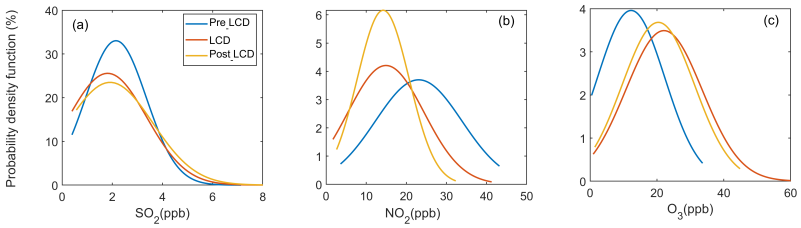

Fig. 4. The probability density function (PDF) of SO2, NO2 and O3 concentration during pre-LCD, LCD and post-LCD, respectively.

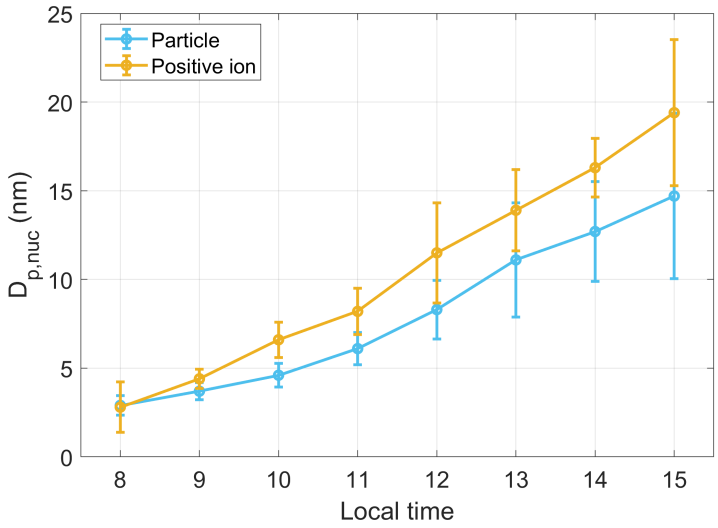

Fig. 5. The time evolution of Dp of nucleation mode (Dp,nuc) of neutral particle and positive charged ions during the NPF events. The circle and bar present the mean and the standard deviation values.

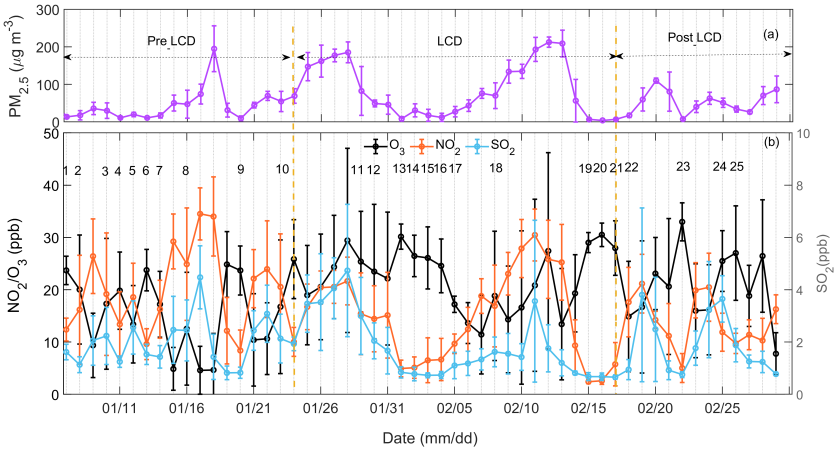

Fig. 6. Concentration level of PM2.5 mass concentration (a), and precursors (b), including NO2, SO2, and O3 during the measurement period.

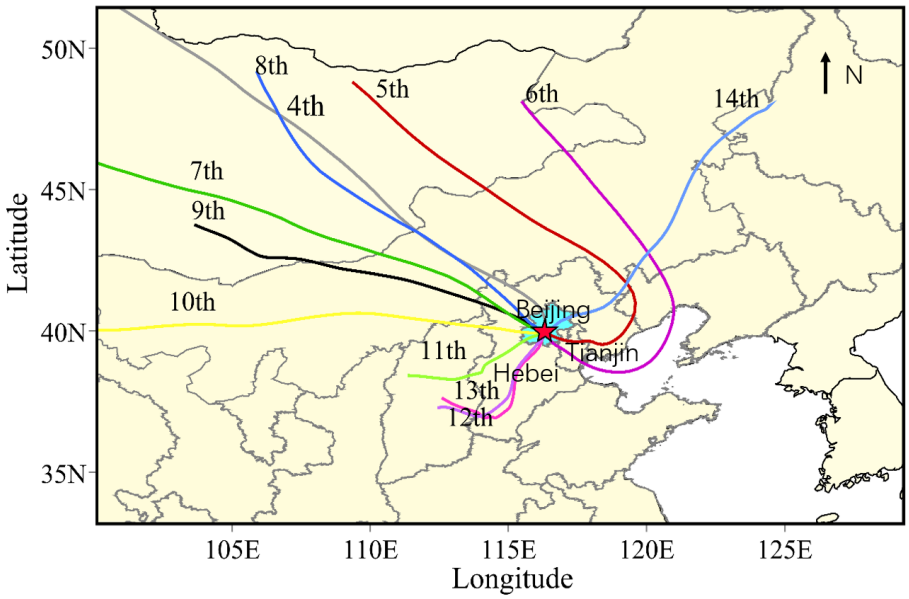

Fig. 7. The back-trajectory arriving at CAMS at 12:00 local time from Feb 4th to 14th, the star indicating the measurement site (CAMS) in Beijing.