

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

**Xiaojing Shen et al.**

shenxj@cma.gov.cn

Received and published: 20 February 2021

This study presents observational results of particle and ions number concentration in Beijing, China during Jan. 24 - Feb. 14, 2020. This period represent the Chinese New year and the COVID-19 lockdown period, therefore suitable for understanding the influence of reduced emission to nanoparticle formation and growth. Although the data set is novel and the main research question it wants to discuss sounds interesting, there are too many important values and discussion in the text which are based on guessing. Overall, I don't recommend this paper to be considered to be published before major reconstruction.

[Printer-friendly version](#)

[Discussion paper](#)



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

1. I would say that the current evidence (No measured or modelled VOCs) does not allow the major conclusion on VOC contribution of particle growth of particles of 10nm-100nm. The only mentioning of VOCs is that reduces by  $\sim 45\%$  in the BTH area, but then they say that low volatility products increased with a VOCs oxidation capacity factor of  $\sim 1.3$ . But if we do a simple estimation,  $1.3 \times 0.55 = 0.71$ , which would mean the oxidation products would not increase. I'm not questioning the conclusion that oxidation products could increase, but there's just far too less data in this study to support this.

Response: The authors are appreciated for the reviewer's kind advice, and totally agreed that the direct evidence for the enhanced particle growth due to VOCs was not enough. We supplemented five kinds of VOCs (isoprene, benzene, toluene, C8 and C9 aromatics) derived from PTR-MS during the measurement (Fig. 1), which are the indicators of anthropogenic VOC and also could be oxidized to be HOMs, contributing to the growth process. The result showed C8 and C9 aromatics decreased by approximately 20% and 8% during LCD as compared with Pre\_LCD, however, isoprene and toluene were slightly changed, benzene increased by approximately 21% during LCD period. It also suggested the VOCs we focused didn't show the reduction rate as 45% as Huang et al. (2020) reported in BTH region. Moreover, the major oxidants of VOCs (O<sub>3</sub>, OH and NO<sub>3</sub>) all increased during LCD period, indicating the possibility of enhanced HOMs participating the particle growth. Unfortunately, we cannot measure the oxidation products directly, e.g. by CIMS, in this study. And the simulation of oxidation product of VOCs by model is beyond the scope in this work. In the manuscript, we supplemented the measured VOCs data and detailed discussion, the oxidation products by proxy method was canceled as the reviewer suggested. But the oxidants of VOCs were discussed and we put more emphasis on the relationship between proxy sulfuric acid and NPF events.

2. Furthermore, it seems to me at least that authors does not understand the concept of

[Printer-friendly version](#)[Discussion paper](#)

ELVOCs or HOMs correctly. It should be noted that the concept of “ELVOCs” should be used when we don’t have information of the volatility, but only use “HOMS” when we are discussing oxidized VOCs. However, using  $k_1 \cdot [\text{OH}] \cdot [\text{VOC}] + k_2 \cdot [\text{OH}] \cdot [\text{VOC}]$  is certainly not acceptable as a proxy of HOMs. First, this represents the first generation product of oxidized VOCs, and even for  $\alpha$ -pinene oxidation which is the most studied HOMs production pathway, this only produces very volatile OVOCs, and they won’t contribute substantially for the growth of Aitken mode particles. Secondly, while this proxy was developed for an  $\alpha$ -pinene rich boreal forest, the main VOCs in Beijing are aromatic, alkenes, and even the main BVOC are not a monoterpene but isoprene. So there needs to be far more discussion to settle down which is the main OVOC contributing as low volatile products, and multi-generation products instead of first-order products should be considered. Last but not least, in the wintertime in Beijing, the night is very long, and oxidation by  $\text{NO}_3$  should not be ignored.

Response: Thanks for the constructive comments. The authors have checked the manuscript to correct the terminology. The highly oxygenated organic molecules (HOMs) have been proved to be important for NPF. However, the direct measurement of HOMs is lacking in this work, and the simulation or determination of which VOCs can be oxidized to form low volatile products and contribute to the particle growth is complex and beyond the scope of this study. The effect of HOMs on nucleation and its following growth will be conducted further by applying CIMS in the further study. As explained above, the anthropogenic VOCs measurement data was supplemented in the text. The major pathways of HOMs formation are the oxidation by  $\text{O}_3$ , OH and  $\text{NO}_3$  radicals (Atkinson and Arey, 2003).  $\text{O}_3$  increased by 80% during LCD period. We used Glob\_R as a simple proxy of OH, and Glob\_R increased by ~24% during LCD as compared with pre-LCD. Thanks for the reviewer providing the new sight that the oxidation by  $\text{NO}_3$  is a key process of night chemistry. It has been reported the monoterpene oxidation initiated by  $\text{NO}_3$  played an important role for HOMs formation in boreal forest, especially in winter time (Yan et al., 2016; Kontkanen et al., 2016). In urban Beijing,  $\text{NO}_3$  oxidation of nocturnal BVOCs is also an important pathway of SOA formation

[Printer-friendly version](#)[Discussion paper](#)

in summer time (Wang et al., 2018). However, the estimation of the multi-generation of VOCs product by NO<sub>x</sub> oxidation needs to be conducted by applying model and more measurement data, which is not available in this work and the simple proxy can introduce large uncertainties. NO<sub>3</sub> is predominantly formed by the reaction of NO<sub>2</sub> with O<sub>3</sub> (NO<sub>2</sub>+O<sub>3</sub>→NO<sub>3</sub>+O<sub>2</sub>), and we applied [NO<sub>2</sub>]\*[O<sub>3</sub>] to estimate the NO<sub>3</sub> production term. It showed [NO<sub>2</sub>]\*[O<sub>3</sub>] term increased by ~40% during LCD period, indicating the possibly enhanced oxidizing products of VOCs by NO<sub>3</sub> during the nighttime. We also supplemented the discussion in the manuscript.

#### References:

Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, *Atmos. Environ.*, 37(Supplement No. 2): S197–S219, 2003.

Yan, C., Nie, W., Äijälä, M., Rissanen, M. P., et al.: Source characterization of highly oxidized multifunctional compounds in a boreal forest environment using positive matrix factorization, *Atmospheric Chemistry and Physics*, 16(19): 12715-12731, 2016.

Kontkanen, J., Paasonen, P., Aalto, J., Bäck, J., Rantala, P., Petäjä, T. and Kulmala, M.: Simple proxies for estimating the concentrations of monoterpenes and their oxidation products at a boreal forest site, *Atmos. Chem. Phys.*, 16(20): 13291-13307, 2016.

Wang, H., Lu, K., Guo, S., Wu, Z., Shang, D., Tan, Z., Wang, Y., Le Breton, M., Lou, S., Tang, M., Wu, Y., Zhu, W., Zheng, J., Zeng, L., Hallquist, M., Hu, M. and Zhang, Y.: Efficient N<sub>2</sub>O<sub>5</sub> uptake and NO<sub>3</sub> oxidation in the outflow of urban Beijing, *Atmospheric Chemistry and Physics*, 18(13): 9705-9721, 2018.

3. The authors claim that nucleated particles can grow to CCN size and contribute to particle mass during haze events. But overall, there is very less discussion of investigation of the particle growing from nucleation mode to accumulation mode, which means that quantitative understanding is lacking. For Fig7., if we take 6th Feb for ex-

[Printer-friendly version](#)[Discussion paper](#)

ample, it seems that the growth from aitken to accumulation mode comes from growth of pre-existing particles. And even though the growth of particle number concentration seems to terminate by 7th Feb, it seems that the PM<sub>2.5</sub> mass still increases rapidly. At noon 8th Feb, it looks like there is a new polluted air mass coming, leading for stronger pollution.

Response: The 48 hours back-trajectory analysis from February, 4th-14th, corresponding to the polluted case study period, which is also supplemented in the manuscript. The back trajectories originated from northwest from February 4th to 10th (Fig. 2), corresponding to the dry and clean air masses. 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 PM. The NPF events both occurred on February 4th and 5th, producing high number concentration of nucleated particles. On 5th and 6th, the air masses passed through Tianjin, which was a megacity in the south-east of Beijing, containing the anthropogenic gases and could favor the NPF growth process. The nucleated particles grew into the larger sizes in the following days until February 10th. On Feb 7th to 9th, the air masses all originated from northwest, and the variation of PM<sub>2.5</sub> could be caused by the planetary boundary layer (PBL) mixing on Feb 8th. Moreover, the variation of local wind could also disturb the growth process. The PM<sub>2.5</sub> normalized by CO also showed an increasing trend from February 4th to 10th, indicating a strong secondary aerosol formation.

4. I think the paper can be resubmitted by putting more effort on nucleation and early growth by sulfuric acid. The NAIS measurement seems to work good, and could be discussed more in depth. To explain the growth driven by oxidized VOCs, either support by measurement of chemical composition or a chemical mechanism model is needed.

Response: (1) The influence of sulfuric acid on the growth process was further analyzed as the reviewer suggested. Based on the NAIS data of neutral particle mode, the hourly mean geometric mean diameter of nucleation mode ( $D_{p,nuc}$ ) was fitted to show the growth process. The result showed much higher proxy sulfuric acid concentration

[Printer-friendly version](#)[Discussion paper](#)

[H<sub>2</sub>SO<sub>4</sub>] during the LCD and post-LCD period, as compared with the pre-LCD period (Fig. 3). It also revealed that in the initial growth process ( $D_{p,nuc} < 5$  nm),  $D_{p,nuc}$  increased positively with [H<sub>2</sub>SO<sub>4</sub>]. Furthermore, GR in the size range of 3-5 nm was slightly higher during LCD and post-LCD (0.72 nm/h), as compared with pre-LCD (0.60 nm/h), indicating the enhanced effect of sulfuric acid on the initial growth of the nucleated particles. However, when the nucleated particles grew into the larger sizes (> 5 nm), [H<sub>2</sub>SO<sub>4</sub>] decreased probably related with the weakened solar radiation wintertime, which could not explain the continuous growth and the VOCs could be the main contributor. As the reviewer recommended, we should have more discussion about NAIS data in details. The mean time evolution of  $D_{p,nuc}$  of neutral particles ( $D_{p,nuc,par}$ ) and charged ions ( $D_{p,nuc,ion}$ ) during the NPF events was given in Fig. 4. It showed  $D_{p,nuc,ion}$  grow faster than  $D_{p,nuc,par}$ , especially for the sizes below 10 nm, depending on the growth rate in each time interval ( $(D_{p,nuc,t1} - D_{p,nuc,t2})/\Delta t$ ,  $\Delta t = 1$  h). The enhanced growth rate factor ( $GR_{p,nuc,ion}/GR_{p,nuc,par}$ ) ranged from 1.1 to 1.7, with the average of  $1.38 \pm 0.34$  during the entire particle growth process and higher ( $\sim 2.0$ ) for the initial size of 2–5 nm.

(2) The times series of isoprene and major C<sub>6</sub>–C<sub>9</sub> VOCs observed in this study by PTR-MS and the PDF distribution were given in Fig. S1. These VOC gases are too volatile to participate in nucleation or growth, they are good indicators of anthropogenic VOC plumes (Dai et al., 2017). It is possible that these plumes contained high concentrations of ammonia, amines, or HOMs produced from these VOCs, which are potential drivers of strong local NPF events. As compared with Pre\_LCD period, the mean average of isoprene and toluene were slightly changed during LCD, C<sub>8</sub> and C<sub>9</sub> decreased by 20% and 8%, respectively, and the mixing ratio of benzene increased by approximately 21% during LCD period. However, the oxidized VOCs (HOMs) are difficult to be evaluated in this work.

Dai, L., Wang, H., Zhou, L., An, J., Tang, L., Lu, C., Yan, W., Liu, R., Kong, S., Chen, M., Lee, S. and Yu, H.: Regional and local new particle formation events observed in

[Printer-friendly version](#)[Discussion paper](#)

the Yangtze River Delta region, China, *J. Geophys. Res.*, 122(4): 2389-2402, DOI: 10.1002/2016jd026030, 2017.

Minor comments:

1. The fitting coefficients for H<sub>2</sub>SO<sub>4</sub> proxy should not used the same as the measurement in Finland. For Beijing, there's a paper by Lu et al (2019). Note that the effect is nonlinear and will effect trend in Fig 4-5. And if Global Radiation is used instead of UVB for H<sub>2</sub>SO<sub>4</sub>, it should be stated as it was done for OH. UVB is a fraction of Global Radiation, therefore a new coefficient should be used. Lu, Y., Yan, C., Fu, Y., Chen, Y., Liu, Y., Yang, G., Wang, Y., Bianchi, F., Chu, B., Zhou, Y., Yin, R., Baalbaki, R., Garmash, O., Deng, C., Wang, W., Liu, Y., Petäjä, T., Kerminen, V.-M., Jiang, J., Kulmala, M., and Wang, L.: A proxy for atmospheric daytime gaseous sulfuric acid concentration in urban Beijing, *Atmos. Chem. Phys.*, 19, 1971–1983, <https://doi.org/10.5194/acp-19-1971-2019>, 2019.

Response: Thanks for the constructive comments, we re-calculated proxy H<sub>2</sub>SO<sub>4</sub> by Lu et al., (2019) and did the reanalysis. In the new calculation of [H<sub>2</sub>SO<sub>4</sub>] in Beijing, we chose proxy equation number 2 (Eq. 1) and 7 (Eq. 2) as recommended by Lu et al. (2019), to represent the simplest and most accurate method, respectively.

$$[\text{H}_2\text{SO}_4]=280.05\times\text{UVB}^{0.14}\times[\text{SO}_2]^{0.40} \quad (1)$$

$$[\text{H}_2\text{SO}_4]=0.0013\times\text{UVB}^{0.13}\times[\text{SO}_2]^{0.40}\times\text{CS}^{(-0.17)}\times([\text{O}_3]^{0.44}+[\text{NO}_x]^{0.41}) \quad (2)$$

And the UVB was derived by  $0.008\% \times \text{Glob\_R}$ , 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 February (0.008%) was applied. However, the results derive by N2 and N7 method (Lu et al., 2019) showed a clear difference, indicating the large uncertainty of the proxy method. And for several NPF events, the elevated concentration of sulfuric acid was not observed by N2 and N7 method. The main reason could be the role of CS was under-

estimated. In the previous study in Beijing (Lu et al., 2019), the covariance of CS and SO<sub>2</sub> was found (correlation coefficient  $R=0.83$ ) that offset the dependence of sulfuric acid on CS. However, during the measurement in our study, a special period of emission sharply decreased,  $R$  is 0.45 between SO<sub>2</sub> and CS. As a compromise, we also referred the proxy method developed in boreal forest (Petäjä et al., 2009). The average value of three proxy methods was applied to analyze the variation of sulfuric acid and its relationship with NPF events (Fig. 5).

2. I didn't find the OH proxy used here in Petäjä et al (2009). Please make sure the right reference is cited.

Response: the correct citation should be "Nieminen, T., Keronen, P., Asmi, A., Petäjä, T., Määttä, M. D., Kulmala, M. and Kerminen, V.-M.: Trends in atmospheric new-particle formation: 16 years of observations in a boreal-forest environment, *Boreal Environ. Res.*, 19 (suppl. B): 191–214, 2014."

3. There are spelling mistakes and grammar errors, try to find an English expert to fix them all, eg: The number concentration of Aitken mode particles (~25-100nm) should also decrease as expected -> The number concentration of Aitken mode particles (~25-100nm) decreased as expected or The number concentration of Aitken mode particles (~25-100nm) decreased as they should.

Response: The spelling and grammar have been checked through the manuscript, which has been language edited by the English native speakers. The sentence that the reviewer mentioned has been revised to be "The number concentration of Aitken mode particles (~25-100 nm), which is related with the traffic emission (Deventer et al., 2018) is also expected to decrease."

4. Use the term oxidizing capacity consistently, replace all "oxidization capacity"

Response: It has been revised as the reviewer suggested.



2020.

ACPD

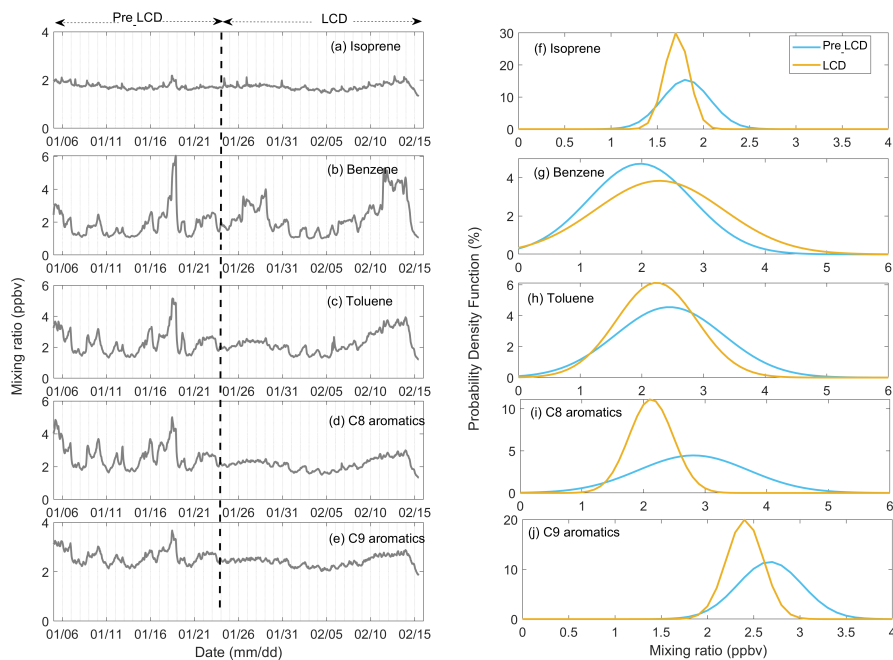
---

Interactive  
comment

Printer-friendly version

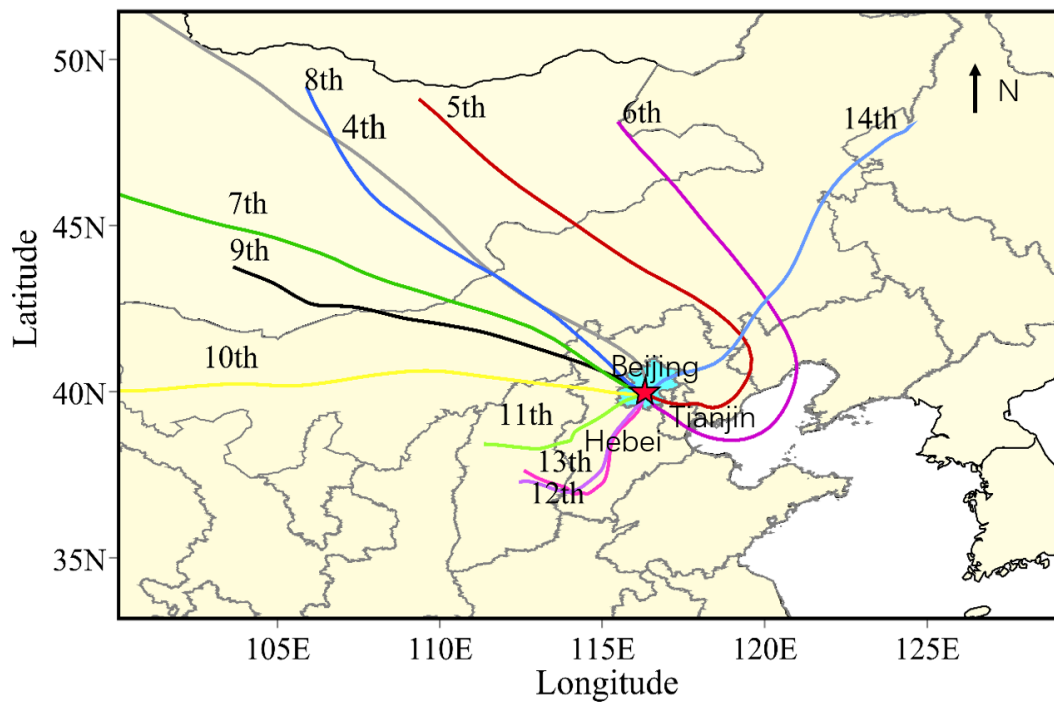
Discussion paper





**Fig. 1.** Time series of isoprene, benzene, toluene, C8 and C9 aromatics (a-e) during January 5 to February 15, and the probability distribution function of mixing ratio of each VOC component (f-j).

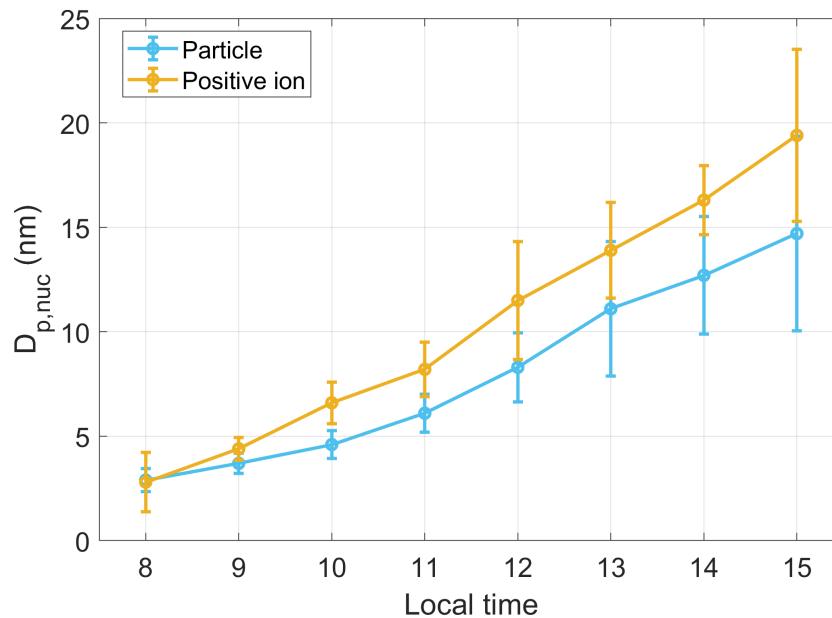
[Printer-friendly version](#)[Discussion paper](#)



**Fig. 2.** The 48 h back-trajectory arriving at CAMS at 12:00 local time from February 4 to 14, the star indicating the measurement site (CAMS) in Beijing.

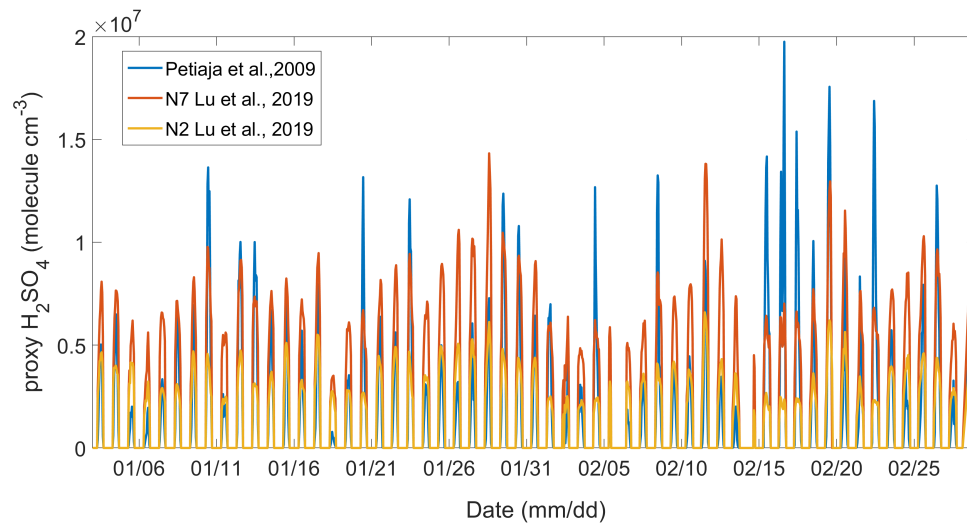
[Printer-friendly version](#)[Discussion paper](#)





**Fig. 4.** The time evolution of geometric mean diameter of nucleation mode ( $D_{p,nuc}$ ) of neutral particle and positive charged ions during the NPF events.

[Printer-friendly version](#)[Discussion paper](#)



**Fig. 5.** The sulfuric acid concentrations derived by different proxy equations.

Printer-friendly version

Discussion paper

