

## Referee #2

This paper presents gas phase sulfuric acid measurements from Beijing during winter and summer with CIMS and show some nighttime formation of sulfuric acid, possibly from sCI formed from VOCs ozonolysis reactions. Sulfuric acid measurements are valuable – considering roles of sulfuric acid on new particle formation especially in urban environments. But data analysis is not effective – please see comments below. The other conclusion is nighttime sulfuric acid is responsible for sub-3 nm particles. How did the authors exclude HOMs from sub-3 nm particle formation?

We thank the reviewer for the constructive comments and suggestions and we have carefully revised our manuscript and supplement accordingly. The point-to-point response to the comments is given below. The comments, our replies, and the corresponding changes in the manuscript and supplementary information are in black, blue, and green, respectively. In this study, HOMs are not likely the determining species for the formation of sub-3nm particles and detailed discussions are shown in the response to question ‘3’.

1) Section 4.3. I have never seen a kinetic expression like this:  $k_{app} \cdot [\text{Alkene}] \cdot [\text{O}_3] \cdot [\text{SO}_2]$ . This does not make sense to me. Please show how  $k_{app}$  is the same as  $k_1 \cdot k_2 \cdot \phi \cdot f$ ? And what about  $k_3$ ,  $k_4$  and  $k_5$  then? Does this mean nighttime sulfuric acid is not from OH + SO<sub>2</sub> reaction (OH from VOCs ozonolysis)? The authors assume are really from sulfuric acid clusters?

Response: Both sCI and non-photochemical ·OH are capable of oxidizing SO<sub>2</sub> to form SA at night. Actually, the contribution of sCI and OH radical cannot be distinguished in our study, and  $k_{app}$  expressed by  $k_1 \cdot k_2 \cdot \phi \cdot f$  in the original manuscript was used to roughly get an upper limit of the sCI oxidation pathway by assuming the contribution of OH radical is negligible. But we found this part of discussion caused much confusion and decided to remove it from the revised manuscript.

The  $k_{app} \cdot [\text{Alkene}] \cdot [\text{O}_3] \cdot [\text{SO}_2]$  is an informal expression of describing the formation rate of SA, where  $k_{app}$  is an overall empirical parameter that takes into account the OH radical and sCI oxidation pathways resulted from the ozonolysis of alkenes. We use this empirical parameter because the detailed chemical formation pathways and corresponding parameters from alkenes, O<sub>3</sub> and SO<sub>2</sub> to SA are still not fully quantified yet.

To clarify this consideration, the following illustration are added to the revised manuscript:

“The ozonolysis of alkenes under dark conditions is capable of generating sCI as well as OH radical, both of which are able to oxidize SO<sub>2</sub> to form gaseous SA. However, the yields of both sCI and recycled OH radical remain largely unquantified. Therefore, we do not attempt to distinguish the contribution of sCI and OH radical on SA formation in this study, but rather treat them as a “bulk oxidant” and use an empirical parameter  $k_{app}$  to account for both oxidation pathways.” (Line 205-209, Page 8)

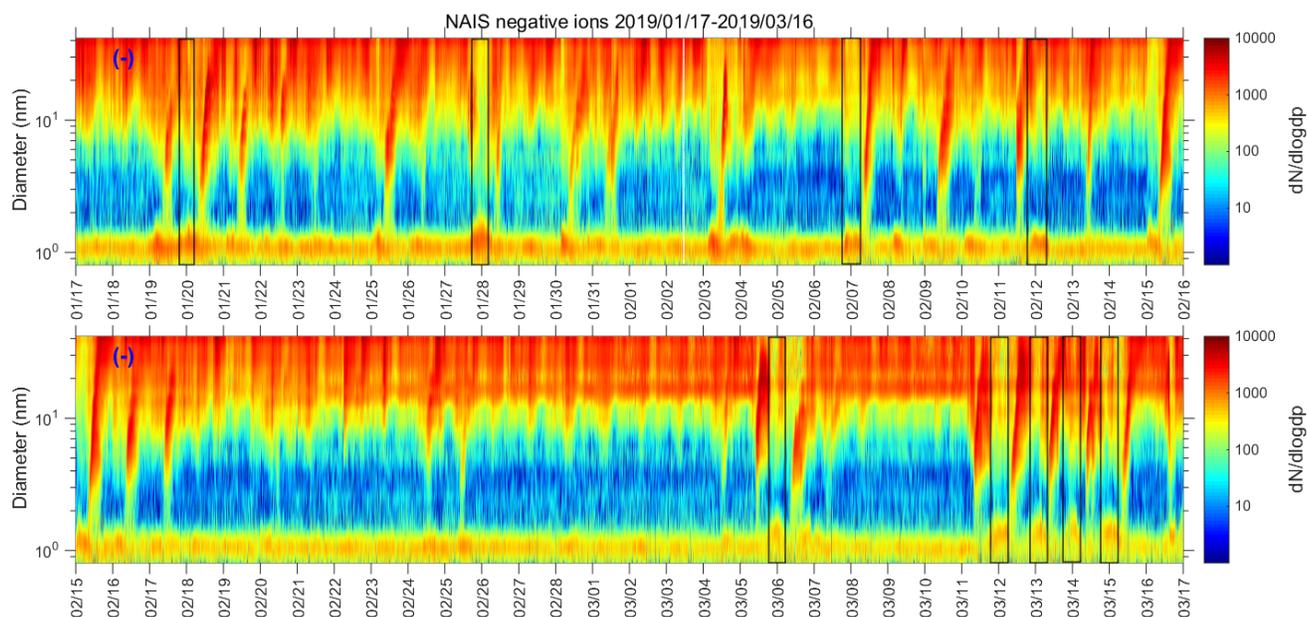
And the following discussion are deleted from the revised manuscript:

“In order to have a general understanding of the apparent rate constant of sCI-SO<sub>2</sub> reaction obtained from our measurement, we can roughly get an upper limit value by considering all nighttime SA is produced from the sCI mechanism. From the above discussion, the slope  $k_{app}$  can be expressed as  $k_1 \cdot k_2 \cdot \phi \cdot f$ , where  $f$  is the fraction of sCI which undergo the reaction with SO<sub>2</sub>. It should be pointed out that  $k_2$  is also an apparent rate constant which results from the combination of different measurement efficiency of alkenes (including undetected ones), different yields of sCI, and different rate constants of sCI reacting with SO<sub>2</sub>. The fitted  $k_{app}$  is  $2.618 \times 10^{-30} \text{ cm}^6 \text{ s}^{-2}$ . If considering  $k_1$  to be  $1.0 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$  (an intermediate value in the range of previous studies, which has been explained in Section 2), then  $k_2 \cdot \phi \cdot f = 2.618 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ . As the real atmospheric chemical composition is far more complex than experimental ones, the value of  $\phi \cdot f$  should be smaller. Thus, if further considering  $\phi \cdot f$  to be 0.05, then the rate constant  $k_2$  in this real atmospheric condition is approximate  $5.236 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , which is in the same order of magnitude as measured values in experiments (see Section 2).” (between Line 234 and Line 235, Page 9)

The reviewer also asked that “The authors assume are really from sulfuric acid clusters?”. Does the reviewer mean to ask that “Is the nighttime sub-3nm particles are formed from SA clusters?”. And our answer is yes. As shown in Fig. 6 (please note that original Fig. 5 now is Fig. 6), there was a positive linear correlation between  $N_{\text{sub-3nm}}$  and SA, suggesting that SA was the main driving species for sub-3nm particles formation. Detailed discussion on the formation mechanism of sub-3nm particles is shown in response to comment ‘3’ and ‘4’.

2) Please also include size distributions to show if there are new particle formation or not during the night.

Response: As particles measured by PSM only cover the size range of 1.3 nm to 2.45 nm, which is not able to show whether there is new particle formation or not, we plotted the size distribution of negative ions measured by neutral cluster and air ion spectrometer (NAIS) (Fig. R2). In general, among 57 nights from 18<sup>th</sup> January to 15<sup>th</sup> March 2019, there were 9 nights with elevated sub-3nm ions (marked with black rectangles in Fig. R2), but further growth of sub-3nm clusters was not observed.

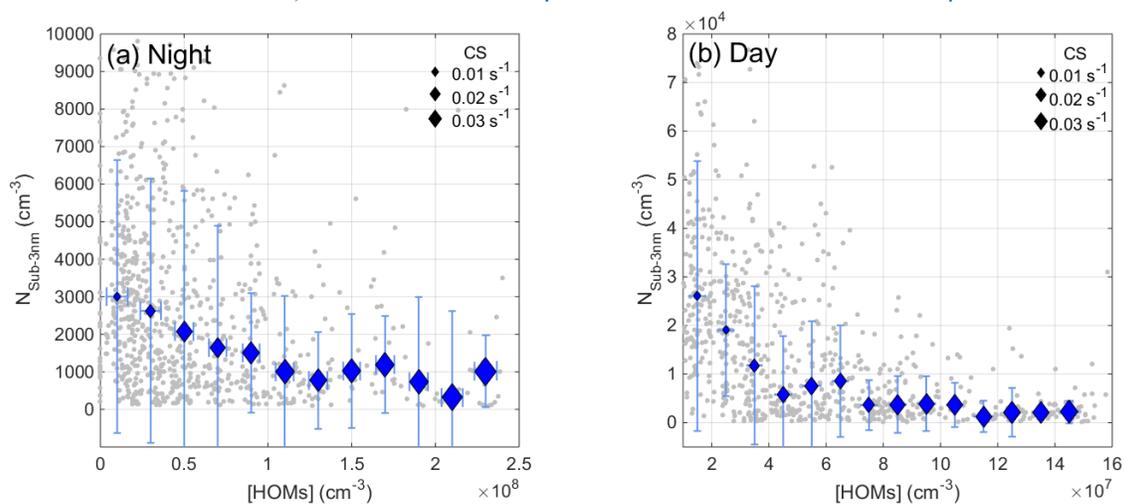


**Fig. R2** Size distribution of negative ions (measured by NAIS) from 17<sup>th</sup> January to 16<sup>th</sup> March 2019. Nights with elevated sub-3nm negative ions are marked with black rectangles. The size distribution of positive ions is similar to that of negative ions and therefore are not shown here.

3) Figure 5. Please also show HOMs in the same way as sulfuric acid, and include day-time data as well (vs. nighttime). Did sub-3 nm particles grow further? If they did not grow larger, then what are the possible explanations?

Response: The correlation between  $N_{\text{Sub-3nm}}$  and concentration of HOMs for both day and night are shown below (and have been added to supplement as Fig. S8).

There was a negative relationship between  $N_{\text{Sub-3nm}}$  and HOMs for both nighttime and daytime, indicating that HOMs were not the main driver for the formation of sub-3nm particles. This phenomenon is in contrast with some previous observations in forested areas where oxidation products of biogenic VOCs, especially monoterpene, were the main contributor to the formation of clusters (Eerdekens et al., 2009; Lehtipalo et al., 2011; Kammer et al., 2018; Rose et al., 2018). Both observation (Rose et al., 2018) and laboratory experiment (Lehtipalo et al., 2018) have shown that HOMs dimers with extremely low volatility play a key role in the initial formation of clusters, while at our site, the high level of  $\text{NO}_x$  inhibited the production of HOM dimers and almost all HOMs are monomers, which are of minor importance to the formation of sub-3nm particles.



**Fig. S8** Correlation between  $N_{\text{Sub-3nm}}$  and  $[\text{HOMs}]$  for (a) during nighttime (20:00-04:00) and (b) during daytime (09:00-16:00) from 18<sup>th</sup> January to 16<sup>th</sup> March 2019. Grey dots are original data, and diamonds are binned ones colored by SA concentration. The size of the binned data is proportional to CS and blue lines are standard deviation of each binned data.

To clarify this consideration, we added Fig. S8 in the revised supplement and the following interpretation in the revised manuscript:

“Different from SA, there was a negative correlation between the concentration of highly oxygenated organic molecules (HOMs) and  $N_{\text{Sub-3nm}}$  for both nighttime and daytime (see Fig. S8 in the supplement), indicating that HOMs were not the main driver for the formation of sub-3nm particles. This phenomenon is in contrast with some previous observations in forested areas where oxidation products of biogenic VOCs, especially monoterpene, were the main contributor to the formation of clusters (Eerdekens et al., 2009; Lehtipalo et al., 2011; Kammer et al., 2018; Rose et al., 2018). Both observation (Rose et al., 2018) and laboratory experiment (Lehtipalo et al., 2018) have shown that HOM dimers with extremely low volatility play a key role in the initial formation of clusters; however at our site in urban Beijing, high level of  $\text{NO}_x$  inhibited the production of HOM dimers and most HOMs are monomers, which have minor importance to the formation of sub-3nm particles.” (Line 272-281, Page 11)

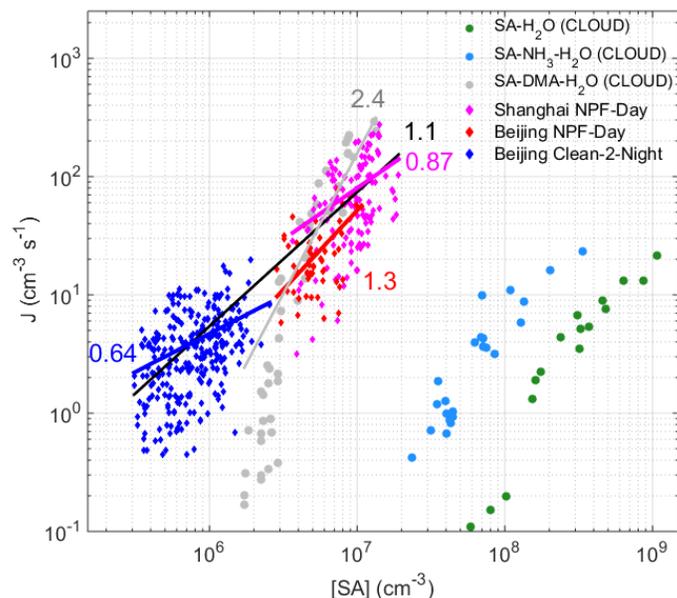
As also shown in Fig. R2, these newly formed particles during the nighttime events are not able to grow to larger sizes. A similar phenomenon was also observed in a Finnish boreal forest (Rose et al., 2018). The reason remains unclear. But the hypothesis is that there is lacking of photochemistry and enough production of essential vapors that dominate the particle growth.

4) Can you calculate J from PSM? What is p (power dependence) of J or sub-3 nm particles on nighttime sulfuric acid (vs. daytime)? Is p different during day and night?

Response: Calculating particle nucleation rate (J) from number concentration (N) involves many corrections including the correction of particle growth out of the size range. However, in these nighttime SA events, the determination of particle growth rate is challenging as the “banana shape” is not clear (please also see the reply to comment #2). This is the main reason why we used the number concentration, as a more objective term, instead of the calculated particle nucleation rate in this study.

However, in order to address the reviewer’s concern on the power dependence, we calculated J by ignoring the particle growth correction. The J as a function of SA concentration is plotted in Fig. R1, including the data in our measurement as well as the reported ones in Shanghai measurement (Yao et al., 2018) and the CLOUD chamber experiments (Almeida et al., 2013; Kirkby et al., 2011) as references. As shown in Fig. R1, data points in the nighttime and the daytime are roughly falling on the same line, which also agree well with the data measured in Shanghai and CLOUD chamber SA-DMA- $\text{H}_2\text{O}$  experiment. The similar J – SA relationship between the nighttime and the daytime suggests a similar nucleation mechanism as SA-base clustering.

The p value (fitted using  $J=k[\text{SA}]^p$ ) of nighttime data alone, daytime data alone, Shanghai data alone, as well as all those three data set together are 0.64, 1.3, 0.87, and 1.1, respectively. However, it should be noted that, the p value may also differ significantly due to different cluster loss rate even when the nucleation mechanism is the same and may also be influenced by the more scattered data in the ambient measurement. This can be seen when comparing the p value of SA-DMA- $\text{H}_2\text{O}$  data in the CLOUD experiment ( $p = 2.4$ ) and the data in Shanghai ( $p = 0.87$ ). Therefore, a detailed discussion on p values was not included in this study. In addition, as the calculation of J has the aforementioned uncertainty, we did not include the Fig. R1 in the manuscript.



**Fig. R1** Comparison of Beijing ambient, Shanghai ambient and CLOUD experimental cluster formation rates against SA concentration. Green, light blue and grey dots denote CLOUD  $J_{1.7}$  data for SA-H<sub>2</sub>O, SA-NH<sub>3</sub>-H<sub>2</sub>O and SA-DMA-H<sub>2</sub>O nucleation respectively (Almeida et al., 2013; Kirkby et al., 2011). Magenta diamonds represent Shanghai NPF  $J_{1.7}$  data (Yao et al., 2018). Red and blue diamonds are Beijing  $J_{1.5}$  data for NPF day (10:00-14:00) and Clean-2 night (20:00-04:00), respectively. The red, blue, magenta and black lines are linear fits for Beijing NPF days, Beijing Clean-2 nights, Shanghai NPF days as well as all those three data set together respectively. The grey line is the linear fit for CLOUD SA-DMA-H<sub>2</sub>O experiments.

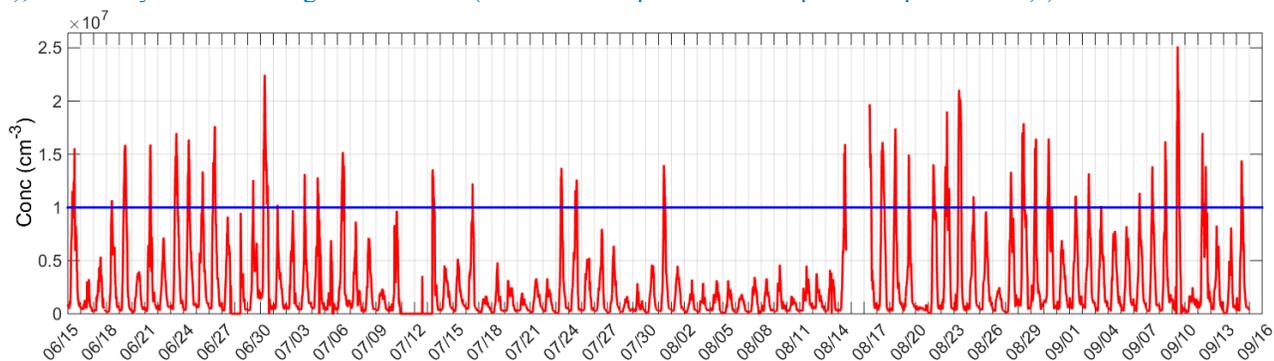
- 5) Line 40: Needs refs., e.g., [Lee et al., 2019].  
 Line 43: Please include [Yu et al., 2012].  
 Line 51: please include [Erupe et al., 2010] and [Yu et al., 2013]

Response: Thanks a lot for your suggestions and we have added these references (Line 40, 43 and 51, Page 2).

- 6) Line 54: needs refs. Is this statement true? I hardly see  $10^7 \text{ cm}^{-3}$  level of sulfuric acid.

Response: Many urban and rural agricultural lands that are dominantly influenced by human activities had daily maximum concentration of SA that was around or exceeded  $1 \times 10^7 \text{ cm}^{-3}$  during summer. Reported places include Hohenpeissenberg in Germany (Birmili et al., 2003), Heidelberg in Germany (Fiedler et al., 2005), Atlanta of Georgia in the US (McMurry et al., 2005), Tecamac in Mexico (Iida et al., 2008), Kent of Ohio in the US (Erupe et al., 2010), Melpitz in Germany (Paasonen et al., 2010), San Pietro Capofume in Italy (Paasonen et al., 2010), Beijing in China (Wang et al., 2011), village of Viebrunn in Germany (Kuerten et al., 2016) and Shanghai in China (Yao et al., 2018). And these references have been added in the revised manuscript (Line 55-56, Page 2).

Besides, the daily maximum concentration of SA at our site during 2019 summer also frequently exceeded  $1 \times 10^7 \text{ cm}^{-3}$  (Fig. R3), which may result from high level of SO<sub>2</sub> (see detailed explanation in response to question '11') and OH radical.



**Fig. R3** Time variation of SA concentration from 15<sup>th</sup> June to 14<sup>th</sup> September 2019. The concentration of  $1 \times 10^7 \text{ cm}^{-3}$  is marked by blue line.

7) Line 60: please include [Yu et al., 2013].

Response: Thanks a lot for your suggestion and we have added this reference (Line 63, Page 2).

8) Line 64: Change “frequent and noticeable” to “noticeable nighttime sulfuric acid sometimes”.

Response: Thanks a lot for your suggestion and we have changed “frequent and noticeable” to “noticeable nighttime sulfuric acid sometimes” as suggested (Line 66-67, Page 3).

9) Line 105: This is a very long inlet. What is the residence time, and radius? Wall loss rate in the inlet?

Response: The length and radius of the inlet of nitrate-LToF-CIMS is 1.6 m and of 3/8 inch respectively. Based on the  $7.2 \text{ L min}^{-1}$  sample flow rate, the residence time is:

$$t = \frac{(\pi \cdot R^2) \times L}{Q} = \frac{3.14 \times (9.525 \times 10^{-3} \text{ m})^2 \times (1.6 \text{ m})}{7.2 \times 10^{-3} \text{ m}^3 \text{ min}^{-1}} \approx 0.0633 \text{ min} \approx 3.80 \text{ s}$$

The SA transport efficiency with diffusional wall loss in the inlet,  $\eta_{SA, \text{inlet}}$ , is calculated according to the Gormley and Kennedy equation (Kulkarni et al., 2011):

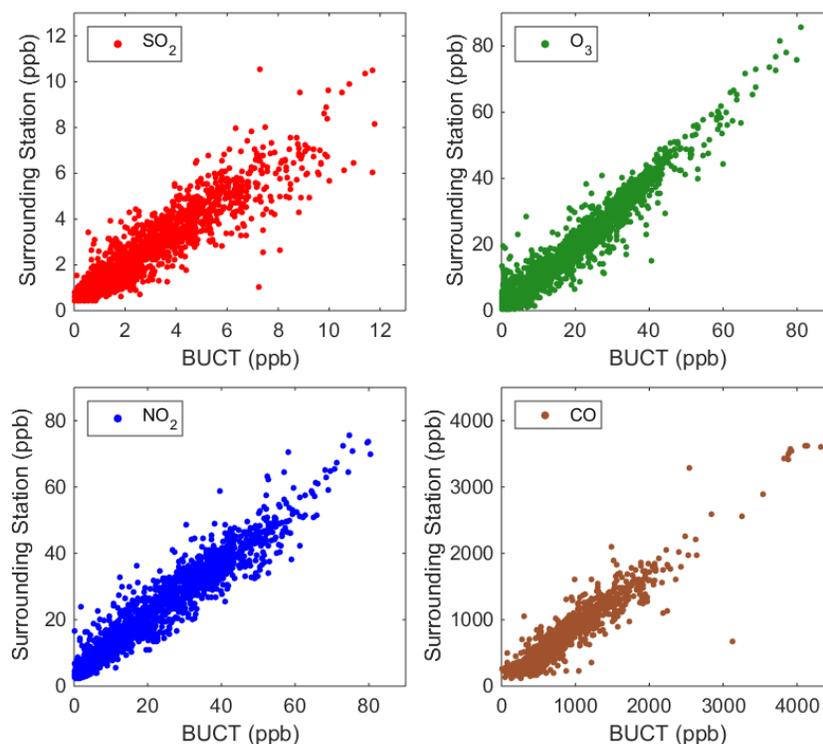
$$\eta_{SA, \text{inlet}} = \begin{cases} 1 - 2.56\xi^{\frac{2}{3}} + 1.2\xi + 0.177\xi^{\frac{4}{3}} & (\xi < 0.02) \\ 0.819 \exp(-3.657\xi) + 0.097 \exp(-22.3\xi) + 0.032 \exp(-57\xi) & (\xi > 0.02) \end{cases}$$

where  $\xi = \pi DL/Q$ ,  $D$  is the diffusion coefficient of gaseous SA (chosen to be  $0.088 \text{ cm}^2 \text{ s}^{-1}$  from (Hanson and Eisele, 2000)),  $L$  is the length of inlet and  $Q$  is the sample flow rate. Then:

$$\begin{aligned} \xi &= \frac{\pi DL}{Q} = \frac{3.14 \times (0.88 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}) \times (1.6 \text{ m})}{(7.2 \times 10^{-3} \div 60 \text{ m}^3 \text{ s}^{-1})} \approx 0.3684 > 0.02 \\ \eta_{SA, \text{inlet}} &= 0.819 \exp(-3.657\xi) + 0.097 \exp(-22.3\xi) + 0.032 \exp(-57\xi) \\ &= 0.819 \exp(-3.657 \times 0.3684) + 0.097 \exp(-22.3 \times 0.3684) + 0.032 \exp(-57 \times 0.3684) \\ &\approx 0.2129 \end{aligned}$$

10) Line 134: Calibration once a month? This is really infrequent! How frequently did they make background measurements?

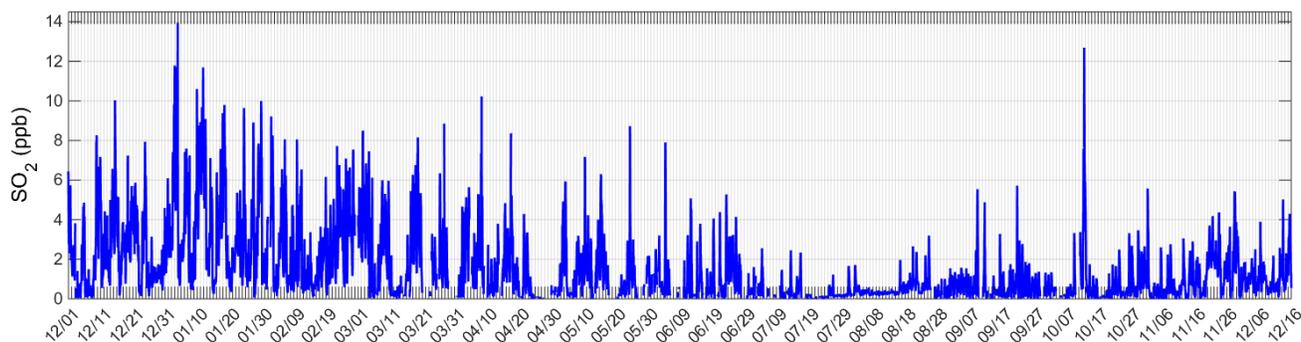
Response: These set of trace gases monitors are very stable. As shown in Fig. R4, measurement of  $\text{SO}_2$ ,  $\text{O}_3$ ,  $\text{NO}_2$ , and  $\text{CO}$  between our BUCT site and surrounding national monitoring stations show a good agreement. So, by doing the multi-point calibration, the data are reliable. And the background measurement is performed along with every calibration experiment by injecting zero air into these instruments.



**Fig. R4** SO<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub>, and CO comparison between our BUCT measurement and the averaged data of four surrounding stations (Gucheng, Haidianwanliu, Guanyuan and Wanshouxigong of China National Environmental Monitoring Center). Time period of data are form 1<sup>st</sup> January to 31<sup>st</sup> March 2019.

11) Line 143/165: Regardless, SO<sub>2</sub> seemed to me always at the ppb in average, so in high SO<sub>2</sub> conditions year around.

Response: Although the restrict control of SO<sub>2</sub> emission has led to noticeable reduction of SO<sub>2</sub> concentration over the recent years, the concentration of SO<sub>2</sub> remains above ppb level, especially in winter due to the operation of heating system and the low boundary layer height (Fig. R5).



**Fig. R5** Time variation of SO<sub>2</sub> from 1<sup>st</sup> December 2018 to 15<sup>th</sup> December 2019.

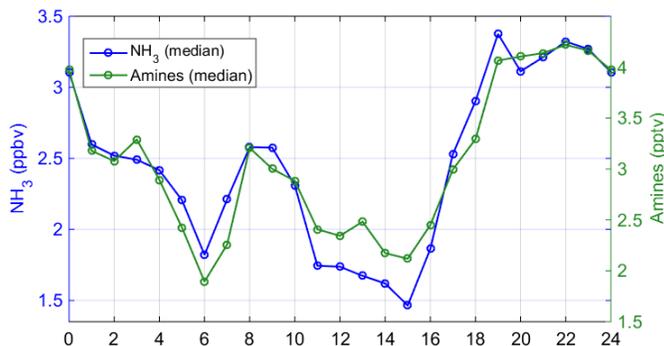
12) Figure 2. Please show amines and ammonia.

Response: Thanks for your suggestion and please also note that Fig. 2 now is Fig. 3.

As we don't have a simultaneous measurements of ammonia (NH<sub>3</sub>) and amines, so that we are not able show the NH<sub>3</sub> and amines difference between SA event and non-event nights. Instead, we plotted the diurnal variation from 10<sup>th</sup> December, 2018 to 6<sup>th</sup> January, 2019 to show the concentration level of NH<sub>3</sub> and amines as well as the variation between day and night (Fig. R6). Accordingly, the median concentrations of NH<sub>3</sub> and C<sub>2</sub>+C<sub>3</sub> amines are also shown in Table R1.

In general, NH<sub>3</sub> and amines had the highest concentration at night (NH<sub>3</sub> ~3.3 ppb,  $8.9 \times 10^{10}$  cm<sup>-3</sup>, amines ~ 4.3 ppt,  $1.2 \times 10^8$  cm<sup>-3</sup>) and the lowest concentration at mid-noon (NH<sub>3</sub> ~1.7 ppb,  $4.6 \times 10^{10}$  cm<sup>-3</sup>, amines ~ 2.3 ppt,  $6.2 \times 10^7$  cm<sup>-3</sup>). Besides, both

NH<sub>3</sub> and amines peaked during the morning rush hour. During nighttime, median NH<sub>3</sub> and amines concentrations were higher under polluted condition (NH<sub>3</sub> ~3.3 ppb, 8.9×10<sup>10</sup> cm<sup>-3</sup>, amines ~ 4.1 ppt, 1.1×10<sup>8</sup> cm<sup>-3</sup>) that those of Clean-2 condition (NH<sub>3</sub> ~1.9 ppb, 5.1×10<sup>10</sup> cm<sup>-3</sup>, amines ~ 2.4 ppt, 6.4×10<sup>7</sup> cm<sup>-3</sup>).



**Fig. R6** Diurnal variation of ammonia (NH<sub>3</sub>) and C2+C3 amines from 10<sup>th</sup> December, 2018 to 6<sup>th</sup> January, 2019.

**Table R1** Median concentrations of NH<sub>3</sub> and C2+C3 amines from 10<sup>th</sup> December, 2018 to 6<sup>th</sup> January, 2019.

| Species         | Unit                              | Night<br>(20:00-04:00) | Day<br>(09:00-16:00) | Polluted Night<br>(Vis < 12 km) | Clean-2 Night (Vis ≥ 16km, [O <sub>3</sub> ] ≥ 2×10 <sup>11</sup> cm <sup>-3</sup> ) |
|-----------------|-----------------------------------|------------------------|----------------------|---------------------------------|--|
| NH <sub>3</sub> | Mixing ratio in ppb               | 2.8                    | 1.7                  | 3.3                             | 1.9  |
|                 | Concentration in cm <sup>-3</sup> | 7.6×10 <sup>10</sup>   | 4.6×10 <sup>10</sup> | 8.9×10 <sup>10</sup>            | 5.1×10 <sup>10</sup>   |
| C2+C3 Amines    | Mixing ratio in ppt               | 3.6                    | 2.3                  | 4.1                             | 2.4  |
|                 | Concentration in cm <sup>-3</sup> | 9.8×10 <sup>7</sup>    | 6.2×10 <sup>7</sup>  | 1.1×10 <sup>8</sup>             | 6.4×10 <sup>7</sup>  |

13) Line 191-192: This does not make sense to me.

Response: The sentence in Line 191-192 of the original manuscript is “A good correlation between source and sink suggests that the assumed source and sink processes are the major factors controlling the SA concentration.”

This sentence is used to illustrate the linear correlation between source term and sink term when there are no additional sources (as the case in Fig 5. (b) for Clean-2 condition), but this sentence is indeed confusing when the source term and sink term are not fully explained in advance. Therefore, we decided to remove it from the revised manuscript as the relationship between the source and sink term has been fully discussed in the following part of Section 4.3.

14) Figure s1: move this to the main text – including spring measurements.

Response: Thanks a lot for your suggestion and we have moved Fig. S1 to the main text as Fig. 1. The time variation of spring measurement (from 20<sup>th</sup> March to 20<sup>th</sup> May 2019) is shown as Fig. S6 in the revised supplement.

15) Figure s3: the same as Figure 3?

Response: They are not the same. Fig. 3 shows the time variation for nighttime SA events occurred under CS decrease condition, while Fig. S3 displays the time variation for nighttime SA events occurred under SO<sub>2</sub> increase condition. Please also note that, Fig. S3 now is Fig. S2 and Fig. 3 now is Fig. 4.

## References

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