Response to the comments of referee II on the driving factors of new particle formation and growth in the polluted boundary layer by Xiao et al.

Xiao et al. make an important contribution on nailing down the different role of precursors and environment factors (mainly temperature) on new particle formation and growth in contrast/diverse conditions in the atmosphere. In their controlled chamber experiments, large variability in NPF rate has been observed, which covers the observed variability in the real atmosphere. The results and conclusion will be very helpful on understanding and interpretating the ambient observations of NPF rates and growth, especially in polluted urban environment. The manuscript is well written, and plots are nicely crafted.

I recommend its publication and have following comments for improvements.

The authors would like to thank the reviewer for the constructive comments, corrections, and suggestions. Here we replied to all the comments and improved the paper following his/her recommendations.

As the main goal of this study is to explain the large variability of the NPF rate in the different environment, it would be nice if the related real atmospheric environment that can be clearly defined, for example, Beijing clean, Madrid, Nanjing, Nanjing Beijing transition, Beijing haze, SE US, SW US, Tartu, Xian, Zurich and so on. I see that the authors have somehow made such attempt by marking them in some plots (e.g., Figure 2A and Figure 5 etc.), but a table of concentrations ranges of the varied precursors, as well as the ambient temperature when the observations were made would be very helpful. I also suggest strengthening a bit the discussion on comparison between chamber conditions and real environmental conditions.

We added a table containing nucleation rates, growth rates, condensation sinks, temperature, and precursors as the reviewer suggests to the SI. Atmospheric parameters span a wide range and we cover this parameter space within the chamber capability to a great extent.

| | J ($cm^{-3}$ $s^{-1}$) | GR (nm $h^{-1}$) | $H_2SO_4$ ($cm^{-3}$) | $NH_3$ | Amine | Org ($cm^{-3}$) | season | Temp (°C) | CS ($s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| Tecamac[a] | 162 (17~2057) | 20 (7.8~>39) | $7\times10^6$-$1.7\times10^7$-$6.6\times10^7$ | | | | end of March to early April | 10-29 | 0.01-0.035 |
| Beijing, Spring[b] | 46.4 (17.7-156) | 2.4 (1.2-3.3 ) | $2\times10^5$-$1.6\times10^6$ | 10 ppb[d] | | | March | 8-24 | 0.0028 (clean), 0.02 (transition), 0.07 (haze) |
| Beijing, Winter[c] | 26(12-38) | 3.5 (0.5-9) | | | | | end of October to January | -15-20 | 0.0042 (0.0023-0.0057) |
| Beijing[e] | 3-100 | | $3\times10^6$-$1\times10^7$ | | 5-32 ppt | | All year round | | 0.017 |
| Nanjing, warm[f] | 92-300 | 1.6-7.1 | $1.3\times10^7$-$3.1\times10^7$ | | | $1.7\times10^7$-$8.5\times10^7$ | | | 0.016-0.019 |
| Nanjing, cold[f] | 190-2500 | 4.2-8.8 | $3.5\times10^7$-$4.8\times10^7$ | | | $1.1\times10^8$-$1.7\times10^8$ | | | 0.028-0.033 |
| YRD[g] | 80 | 12.5 | | | | | winter | | 0.026±0.014 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| SPC[h] | 45 (23-53) | 4.3 (1-10) | | | | | | 20-35 | 0.005-0.025 |
| Madrid[i] | 1.1-6.7 | 2.4-15.7 | | | | | summer | | 3.40E-03 |
| MAJ[i] | 0.7-6.8 | 1.9-8.1 | | | | | | | 2.50E-03 |
| Shanghai[j] | 105 (42-207) | 1.4 (0.55-3.3) | $4\times10^6$-$2\times10^7$ | | ~100 pptv | | All year round | | ~0.02 |
| CLOUD $H_2SO_4$+DMA 278 K[h] | 160-2475 | 1.72-18 | $6.3\times10^5$-$7.6\times10^6$ | 1-2.5 ppb | 4 pptv | HOMs up to $5\times10^7$ OxOrg up to $8.8\times10^9$ | | 5 | 0.002-0.01 |
| CLOUD $H_2SO_4$+DMA 293 K[h] | 2.4-231 | 1.6-6.8 | $1\times10^6$-$7.8\times10^6$ | 1-2.5 ppb | 4 pptv | HOMs up to $8\times10^7$ OxOrg up to $6\times10^9$ | | 20 | 0.002-0.008 |
| CLOUD $H_2SO_4$+$NH_3$ 278 K[h] | 15-537 | 3.2-17.4 | $5\times10^6$-$1.5\times10^7$ | 1-2.5 ppb | Not added | HOMs up to $3\times10^7$ OxOrg up to $9.6\times10^9$ | | 5 | 0.002-0.004 |
| CLOUD $H_2SO_4$+$NH_3$ 278 K[h] | 0.17-27 | 2.4-22 | $7.4\times10^6$-$7.9\times10^7$ | 1-2.5 ppb | Not added | HOMs up to $3\times10^8$ OxOrg up to $9.2\times10^9$ | | 20 | 0.002-0.007 |

[a](Kuang et al., 2008), [b](Cai et al., 2017), [c](Jayaratne et al., 2017), [d](Guo et al., 2017), [e](Cai et al., 2021), [f](Yu et al., 2016), [g](Dai et al., 2017), [h](Kontkanen et al., 2016), [h](Carnerero et al., 2018), [j](Yao et al., 2018), [h]this study.

We have added the following to section 2.3:

"This controlled laboratory exploration spans the relevant ambient conditions, and provides a detailed understanding and constraints of the governing chemical and physical processes of NPF and early growth. This provides the possibility to rationalize the available ambient measurements and a framework to plan future measurements in the best way."

"These conflicting observations are subject of intense scientific debate of late (Brean et al., 2020; Cai et al., 2020; Guo et al., 2020) and highlight…" It would be nice if the authors could elaborate a bit here what are the "scientific debate" here, and I believe it will help the readers to have a better overview and understanding of the motivation of this study.

We added a brief description on the major views of the referenced papers. The modified text reads now:

The high NPF rates, believed to drive haze events in China (Guo et al., 2014), have been associated with the nucleation of sulfuric acid ($H_2SO_4$) in the presence of amines (Yao et al., 2018). In contrast, at other urban locations (Kuang et al., 2008), reported NPF rates are several orders of magnitude lower at similar $H_2SO_4$ concentrations, despite high levels of condensable species able to grow newly formed particles. Cai et al. (2020) attribute NPF in Beijing to $H_2SO_4$-amine cluster formation, which is modulated by coagulation scavenging. In Barcelona, Brean et al. (2020) linked nucleation to sulfuric acid clustering with both highly oxygenated organic molecules (HOMs) and bases, while Guo et al. (2020) argued photooxidation of organics from vehicular exhaust is responsible for the formation of ultrafine particles in Beijing. These conflicting observations and interpretations highlight the need to better understand the role of the different vapours and environmental parameters and

to quantify their relative contribution in new-particle formation and growth in different polluted locations.

I understand that putting the Method section at the end is probably to obey the formatting requirement of letter, the authors may want to refer to sub-sections, descriptions and equations of the Method section in the main text, so the readers could cross check. For example, how are the "Organic fraction of GR" in Figure 4B derived?

We would like to thank the reviewer for this suggestion. We went through the main text and added references to the method section when necessary. In Figure 4 caption, we add "(determined by subtracting GR by sulfuric acid)" to "Contribution of oxidised organics (OxOrg) to sub-3 nm GR".

In Figure 3, organic seems having stronger effects when DMA is absent. Could the authors comment on it?

For clarity, I suggest explaining that "Base" means both NH3 and DMA are present in the figure caption. There is an additional "Figure 3." in the figure caption.

This observation is correct and is mentioned at line 123, where the effect of organics is discussed: "In the presence of amines, the contribution of organics to NPF is marginal, since the inorganic nucleation rate is overwhelming." Since amines are so efficient in stabilizing sulfuric acid, the organic effect becomes marginal. At line 129 it already says: Further addition of organics when DMA is already present will only marginally affect nucleation rates.

"Base" is replaced by "$NH_3$+DMA". We have removed the extra Figure 3.

In Figure 5, survival probability in Beijing haze condition seems extremely low. Here, CS6 is used, and I am wondering how pollute are the Nanjin Beijing transition and Beijing haze condition? E.g., PM1 or PM2.5 concentrations? A related question is that "polluted boundary layer" is with what PM1 or PM2.5 levels approximately?

In Beijing the occurrence of new particle formation is increasingly occurring at a condensation sink lower than 0.03 $s^{-1}$ (Deng et al., 2021). On NPF days a median CS of 0.009 $s^{-1}$ was measured corresponding to a PM2.5 concentration of 10 µg $m^{-3}$. In Nanjing CS is also lower than 0.03 $s^{-1}$ albeit PM2.5 concentrations are higher on NPF days (in spring up to 112 ± 68 µg $m^{-3}$), which could be due to a shift in the particle size distribution to a larger size (Yu et al., 2016). Particle growth to larger sizes is also often not observed.

"Polluted boundary layer" means not only high aerosol concentrations but also other pollutants such as ammonia, amines or volatile vapors. Also "polluted" is a relative term. For example, rural or remote areas could be relatively low in aerosol and anthropogenic organic vapours compared to industrialized/ urban regions, but still polluted due to transport of pollution or agricultural emissions compared to pristine. Thus, PM concentrations in "polluted boundary layer" cover a wide range between a few to tens or hundreds of µg $m^{-3}$.

We added this sentence at the end of the introduction to outline what we mean by polluted boundary layer: The experiments cover low and moderately polluted rural environments as well as highly polluted urban situations.

"We compare chamber simulations and atmospheric observations in Fig. 7 using sub-3 nm GR as a proxy for total condensable vapour concentrations…" It seems that total condensable vapor

concentration in BJ is not high as marked in Figure 7. One would expect that high as the pollution level there is quite high. Could the authors comment on it?

The concentrations of condensable vapours are controlled by their production and sink. While precursor concentrations are high, radiation in Beijing is not as strong as in the southern cities such as Shanghai or Nanjing. High NOx levels also limit the production of extremely low volatility compounds from organic vapours. Sinks of condensable vapours are also high in Beijing since a high pollution level results in a high condensation sink. As a result, the total concentration of condensable vapours is not extremely high in Beijing.

Reference:

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