Response to Reviewer #1 (our response in **colour**)

We thank the reviewer for the constructive comments to help us further improve the manuscript. Please see the detailed responses to your comments below.

Reviewer #1:

The study improved the simulation of aerosol formation processes in the NPF-explicit WRF/Chem model. The amount of work done was impressive. The results are meaningful to aerosol modeling. Overall, the manuscript is well written. However, some details are missing and some expressions need to be revised. I recommend the publication of this work after the following concerns are addressed.

Major comments:

(1) As stated by the authors, new particle formation (NPF) and subsequent particle growth are important sources of condensation nuclei (CN) and cloud condensation nuclei (CCN). NPF is an objective phenomenon and therefore its contribution to CN and CCN is definitely positive. "The nucleation resulted in decreased CCN" is only based on the simulation analysis. The authors should be cautious about the discussions relevant to "negative contribution"

Thanks for the suggestions. We have rephrased the discussions by specifically clarifying the results are from simulations.

(2) When using empirical formulation to calculate nucleation, the overestimation of CN could not be simply attributed to the high prefactor/coefficient in formulation. The empirical formulation has physical flaws because it could not consider the influence of other factors besides sulfuric acid, e.g., temperature and condensation sink.

We agree that temperature and condensation sink are two key parameters affecting nucleation processes, primarily by influencing the level of gaseous precursors involved in the nucleation, and thus the particle number concentration (Zhu et al., 2017). The empirical nucleation parameterizations used in this study is strongly governed by the nucleation coefficient, which indeed is a combination by taking into account the physical and chemical properties of the nucleation process under different environments, including temperature. Some studies have attempted to lower the

nucleation coefficient by an order of magnitude so as to reduce the overestimation of particle number concentration, but overestimation still exists (Matsui et al., 2013; Arghavani et al., 2022; Dong et al., 2019). In contrast, other studies have pointed out the overestimation of particle number concentration is likely induced by too high nucleation precursors such as sulfuric acid (Cai et al., 2016; Matsui et al., 2011). The numerical experiment supported their hypothesis, indicating that accurate simulation of sulfuric acid plays pivotal roles in improving particle number concentrations.

In terms of the reviewer's concern about temperature, previous studies have tested some nucleation schemes by including temperature, and they found that temperature plays a large role when it is high such as over summer, but plays a marginal role under low temperature conditions. Regarding condensation sink, it is taken into account in the current simulations. Specifically, the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) used in this study include dynamic gas-particle mass transfer to represent the condensation growth of aerosol, during which the effect of condensation sink of gases precursors on particles ensures a reasonable level of gas precursors involved in nucleation.

(3) The model bias in this study is only based on the comparison of simulation against measurements at one coastal site. Some discussions may be not applicable to other regions. I suggest that the authors can do some work based on more measurements if possible. At least, discussions on existing modeling studies in China or the influence of factors affecting model performance in other regions of China should be added.

Following your comments, we added two more sites for evaluation, including one site over urban Beijing and the other over the rural area of Gucheng. In addition to Qingdao, we further evaluate the performance of WRF-Chem with updated parameterization of the particle formation and growth processes in reproducing the observed particle number concentrations over a few other sites in the North China Plain, including one site over urban Beijing and the other one over the rural area of Gucheng (see methods in the manuscript). In February 2017, there are 10 and 5 NPF events occurred in Beijing and Gucheng, respectively. The model evaluation based on these two sites in general supports the findings over the site of Qingdao. Specifically, the

simulations using activation-type nucleation mechanism with the mass accommodation coefficient of 0.1 (red lines in Fig. 1), the same as Base in section 3.2.1 in the manuscript, substantially overestimates the number concentration of particles in 10–40 nm. The mean fractional bias of $CN_{10–40}$ in Beijing and Gucheng are 81% and 62% respectively, which is strongly reduced to 23% and 11% by increasing the mass accommodation coefficient of sulfuric acid to 0.65 (see Section 3.2.1 of the manuscript for details).

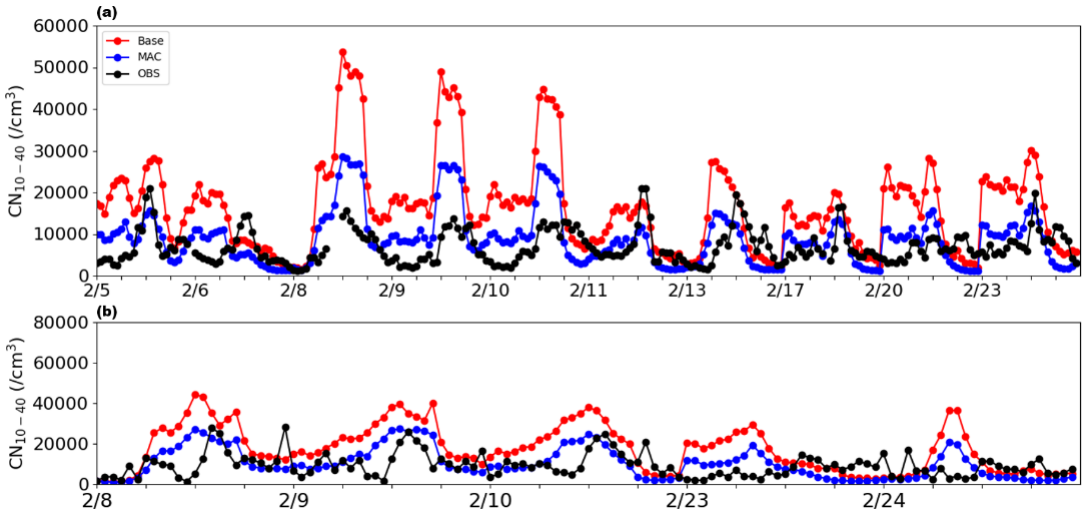

Figure 1 The time series of $CN_{10–40}$ on NPF days in (a) Beijing and (b) Gucheng on February 5-24, where red and blue represent Base and MAC simulation results respectively. All times are local times (LT).

For the larger particles (40–100 nm) which are greatly affected by the condensation process, the relevant parameters are also adjusted. For instance, the modified process includes the amount of nitrate condensation in particles below 40 nm and the emission phase of primary organic aerosol (section 3.2.2 of the manuscript), and the yield of SI-SOA in the model (named Low_yield, see section 3.3 of the manuscript for details). For activation-type nucleation mechanism, the mean fractional bias is reduced from 103% to 59% in Beijing, 50% to -5% in Gucheng, with correlation coefficient increasing from 0 to 0.49 and 0.46. (Figure 2).

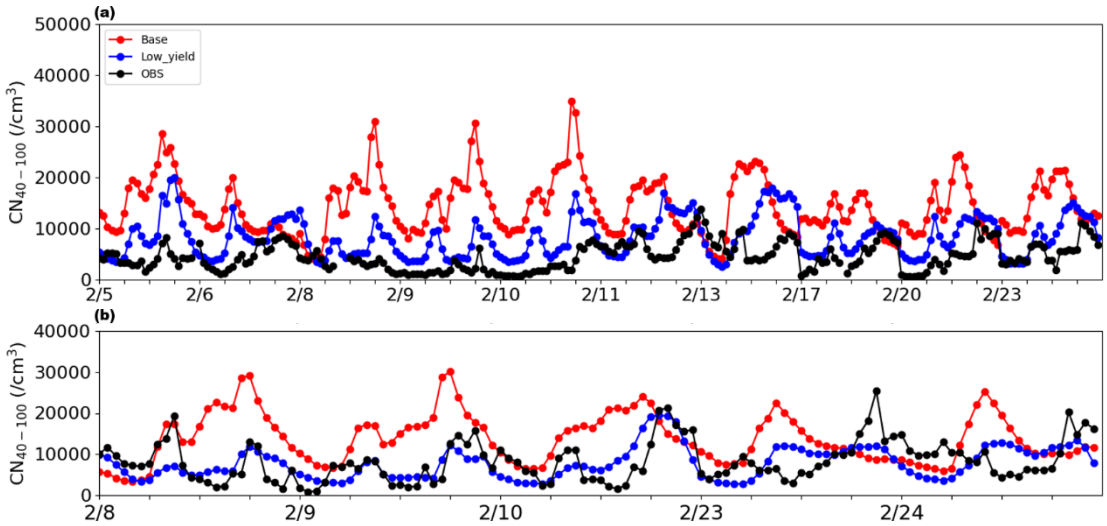

Figure 2 The time series of $CN_{40–100}$ on NPF days in (a) Beijing and (b) Gucheng on February 5-24, where red and blue represent Base and Low_yield simulation results respectively. All times are local times (LT).

(4) The comparison of the simulated mass concentration of aerosol components and gaseous precursors against observations is encouraged to present before evaluating the model performance in CN.

Following your comments, we have added more model evaluations, including $PM_{2.5}$ compositions derived from a near real-time air pollutant database (Tracking Air Pollution in China, http://tapdata.org.cn) (Geng et al., 2017; Liu et al., 2022) such as SO_4^{2-}, NO_3^-, NH_4^+, OM (Fig. 3) and criteria air pollutants, including particulate matter ($PM_{2.5}$ and PM_{10}) and gaseous pollutants (O_3, SO_2, CO, and NO_2) (Fig. 4) in the megacity of Beijing and a coastal city of Qingdao during the simulation period. Overall, relatively low bias is achieved for most of the species.

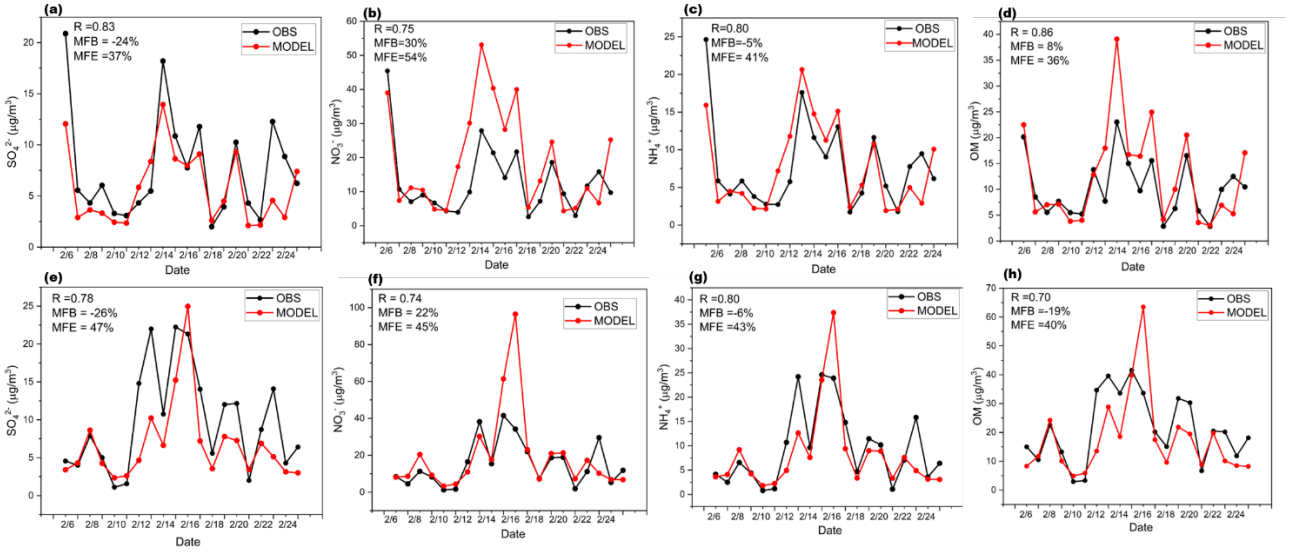

Figure 3 The comparison between model simulations (red lines) and observations (black lines) from February 5 to February 24, 2017. Shown are results of the average daily concentration of the four main components of $PM_{2.5}$ (SO_4^{2-}, NO_3^-, NH_4^+, OM) in Qingdao (top) and Beijing (bottom). Statistical indicators including mean fractional bias (MFB), mean fractional error (MFE) and correlation coefficient (R) are also displayed in the upper left corner of each panel.

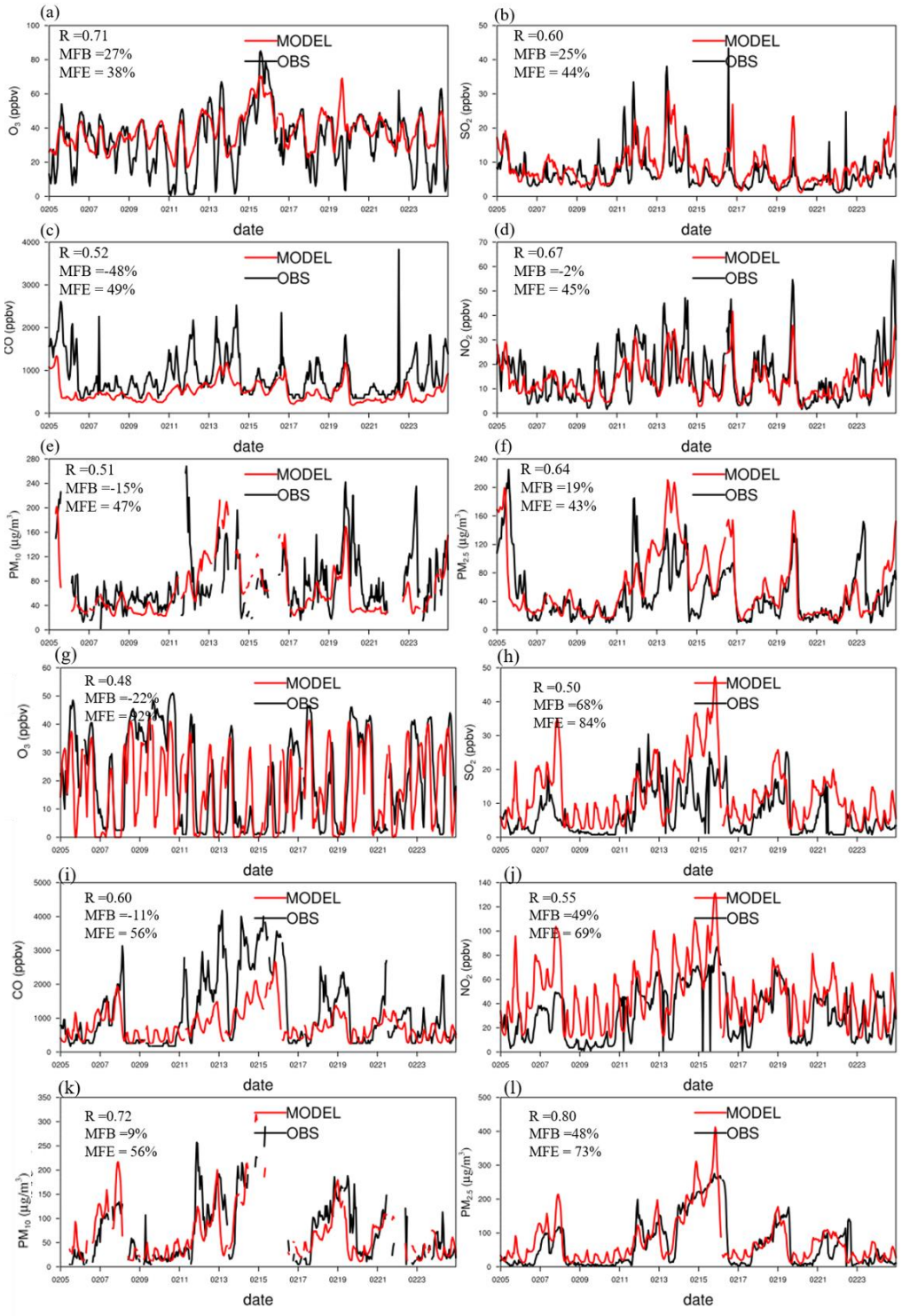

Figure 4 The comparison between model simulations and observations from February 5 to February 24, 2017. Shown are results of concentrations of air pollutants (O_3, SO_2, CO NO_2, PM_{10} and $PM_{2.5}$) in Qingdao (Fig. 5a–f) and Beijing (Fig. 5g–l). Statistical indicators including mean fractional bias (MFB), mean fractional error (MFE) and correlation coefficient (R) are also displayed in the upper left corner of each panel.

(5) The method of calculating CCN is necessary in Sect.2.

According to your comments, we have added the calculation method of CCN in the manuscript. The calculation method of CCN concentration in the WRF-chem model is based on the study of Matsui et al. (2011). According to Köhler theory, CCN concentrations under three given supersaturations of 0.2%, 0.4% and 0.6% were calculated. The critical supersaturation (S_c) of each size bin in the WRF-chem model was calculated by the following formula:

$$S_c = \sqrt{\frac{4 \times a^3}{27 \times r^3 \times \kappa}} \quad (1)$$

$$a = \frac{2 \times \sigma}{R_v \times T \times \rho_\omega} \quad (2)$$

Where α (m) is the coefficient of the Kelvin effect, κ is the volume–averaged hygroscopicity, calculated using the values in Table 1, r (m) is the dry diameter, σ is droplet surface tension over water (0.076 N m^{-1}), R_v is the gas constant for water vapor (461.6 J $K^{-1}kg^{-1}$), T (K) is the air temperature, and ρ_ω is the density of water (1000 kg m^{-3}).

Table 1 Hygroscopicity Parameters (κ) in the WRF-Chem Model

Species	Hygroscopicity (κ)
Sulfate	0.5
Ammonium	0.5
Nitrate	0.5
Black carbon	10^{-6}
Primary organic aerosol	0.14
Other inorganics	0.14
Sodium	1.16
Chloride	1.16

(6) How is the emission of IVOC considered?

In the 2-species volatility basis set (VBS) treatment of secondary organic aerosol formation used in WRF-chem in this study, SVOC and IVOC emissions corresponding

to both anthropogenic and biomass burning emissions are derived based on a constant emission ratio of S/IVOC to POA (Shrivastava et al., 2011). Specifically, the emission of IVOC is assumed to be 6.5 times that of POA, which may have some uncertainty due to different emission ratios of POA from different source, requiring more work in future for the investigation.

(7) Is Knudsen effect considered when calculating the condensation of gases onto nano-size particles?

Yes, the model used in the study takes into account the Knudsen effect when calculating the condensation of gases on particles. Gas-particle partitioning process for various species are delineated using the Model for Simulating Aerosol Interactions and Chemistry scheme (MOSAIC) in the WRF-Chem model. The following formula is used to calculate first order mass transfer coefficient for gaseous precursors on particles, where Knudsen effect is taken into account (Zaveri et al., 2008):

$$K_{i,m} = 4\pi \bar{R}_{p,m} D_{g,i} N_m \mathrm{f}\left(Kn_{i,m}, \alpha_i\right) \quad (3)$$

$$\mathrm{f}\left(Kn_{i,m}, \alpha_i\right) = \frac{0.75\alpha_i\left(1 + Kn_{i,m}\right)}{Kn_{i,m}\left(1 + Kn_{i,m}\right) + 0.283\alpha_i\, Kn_{i,m} + 0.75\alpha_i} \quad (4)$$

Where $k_{i,m}$ (s^{-1}) is the first order mass transfer coefficient for species i and bin m; $\bar{R}_{p,m}$ (cm) is mean wet radius of particles in bin m; $D_{g,i}$ ($cm^2\ s^{-1}$) is gas diffusivity of species i; N_m (cm^{-3}) is the number concentration of particles in bin m; $f(Kn_{i,m}, \alpha_i)$ is the transition regime correction factor to the Maxwellian flux as a function of the Knudsen Number (Fuchs and Sutugin, 1971); α_i refers to the mass accommodation coefficient.

(8) The simplified SOA simulation in this study did not consider the multi-stage oxidation of organic species, which can affect the microphysical properties of organic species in particle growth processes. Discussions on this issue is suggested.

Thank you for your valuable comments. The simplified VBS mechanism used in our study does not consider the multi-step oxidation of organic species, and we have added some elaboration to address the uncertainties.

In the 2-species VBS mechanism used in the study, SI-SOA with effective saturation concentrations (C^*) of 10^{-2} μg m^{-3} is formed by the one-step vapor phase

oxidation of S/IVOC vapors with C^* of 10^5 μg m^{-3} through a reduction of volatility by 7 orders of magnitude. Instead of representing the real physics, this process aims to parameterize the mean effect of the complex processes of SOA formation (Shrivastava et al., 2011), which may potentially underestimate SOA (Chrit et al., 2018; Zhao et al., 2020) concentrations and the subsequent effect on CCN.

(9) The model resolution is not high enough to well resolve the urban pollution. In discussing the model performance, this factor should be taken into account.

We understand that a higher spatial resolution may be desirable when urban pollution is a major concern. In the revised manuscript, we have added two more sites (one over urban and the other over rural area) based on the reviewer's earlier comments, and the model in general shows reasonable performance. We do believe higher spatial resolution simulations may improve the performance if the spatial resolution of emission inventory improves. We have incorporated the factor of resolution into the Method section in the revised manuscript.

(10) Fig.3 shows a different temporal variation of $CN_{10–40}$ from that of $CN_{40–100}$ which shares a similar pattern with that of $CN_{100–1000}$. Primary emission may be a dominant factor contributing to model bias in $CN_{40–100}$. Is the diurnal variation of emission considered in emission data? Correlation coefficient between the simulation results and the observations is recommended to show.

Diurnal variations in emissions are taken into account when processing emission data in the WRF-chem model. Based on the reviewer's comments, we calculated the correlation coefficient and added into Table S1 and S2 in the supporting information.

Technical suggestions:

L191 and L193, organic aerosols -> organic matters

Done

L269, NFP-explicit -> NPF-explicit

Done

In Fig.2 and Fig.3, horizontal label bar is better

Done

Higher and narrower Fig.4 with horizontal label bar is better.

The figure and label have been revised.

In fig.5, a unified color bar for fig.5a, b, and c would be better.

Done

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