We are grateful to the referees for the encouraging comments and careful reviews which helped to improve our paper. The point-by-point responses and corresponding changes within the manuscript are shown below. The comments are in black, and the responses are in blue. The changes within the manuscript are italicized.

Reviewer #1

This paper conducted a very comprehensive investigation of the model simulation of VOC using the Community Multiscale Air Quality (CMAQ) model and compared it with an excellent observation dataset including 28 sites across China. On one hand, they showed an overall underestimation of the VOC concentration, these biases often occurred in industrial cities. On the other hand, this VOC model simulation bias may lead to lower O_3 predictions in China. The gap between VOC model simulation and observation may also influence the diagnosis of ozone production sensitivity regimes and other air pollution problems like the atmospheric oxidation capacity and the secondary aerosol formations. Therefore, I believe this topic is fundamental and critical to the atmospheric science community. This paper is well-written, and the data analysis convinced me. I would like to recommend this paper be published in ACP subject to add more detailed information about the VOC measurement as well as some minor corrections.

1. In the method Section, although the author cited the literature to support the introduction of VOC measurement. However, I strongly recommend that the authors add a more detailed description of measurement techniques and uncertainties, as this part may also greatly affect the comparison of observations and simulations. Considering that there are currently large differences in the consistency between models and observations in different regions, the authors need to clarify further whether VOC observations in all sites have adopted uniform sample-analysis and data quality control standards, in other words, whether these systematic differences may be due to uncertainties in VOC measurements?

Response: Thanks for the comment. We agree that the uncertainties in the VOC measurements are important for interpreting the comparison of VOC measurements and simulations. As you suggested, we added a description of measurement techniques and uncertainties in the main text, with more details in the supplementary information:

Lines 116-128 in the revised manuscript:

The offline measurement techniques, and data quality assurance and quality controls (QA/QC), which were consistent across all sites, have been previously described (Lyu et al., 2019; Lyu et al., 2020; Liu et al., 2021; Zhou et al., 2023). Briefly, stainless steel canisters and 2,4-dinitrophenylhydrazine (DNPH) cartridges were utilized to collect non-methane hydrocarbons (NMHCs) and oxygenated VOCs (OVOCs), respectively. NMHCs were quantified using a gas chromatograph (GC) coupled with a mass

spectrometry detector (MSD), electron capture detector (ECD), and flame ionization detector (FID) (the GC-FID system for C_2-C_3 species, and GC-MSD/ECD for other NMHCs). OVOC samples were analyzed by high-performance liquid chromatography. The accuracies for the NMHC measurements ranged from -22.58%–8.71%, with precisions of 0.86%–25.89% (Zhou et al., 2023). More details regarding the measurements can be found in Supplement S.1.

Lines 8-32 in the supplementary information:

S.1 VOCs measurements

In the ATMSYC project, sampling was conducted in both winter and summer. The VOC measurements from 6 June to 24 August 2018 were employed in this study. Table S1 shows the locations of 28 sites, along with sampling time and the number of VOC samples. The methods for sampling and analyses were consistent across sites. Non-methane hydrocarbons (NMHCs) were collected in 2L stainless steel canisters, and all canisters were cleaned and evacuated at least three times with zero air before sampling. During the sampling, flow restrictors were used to guarantee that each sample lasted for one hour (Lyu et al., 2019; Lyu et al., 2020). Oxygenated VOCs (OVOCs) were sampled with 2,4-dinitrophenylhydrazine (DNPH) cartridges with O_3 scrubbers installed in front of them to remove airborne O_3. The sampling duration of OVOC was 2 h and the sampling flow rate was fixed at 0.5 L/min. All the DNPH cartridges were stored in a refrigerator at 4 ℃ before the chemical analyses (Lyu et al., 2019; Lyu et al., 2020).

The NMHC species were identified and quantified by gas chromatography coupled with a mass spectrometry detector, electron capture detector, and flame ionization detector at Hong Kong Polytechnic University (Lyu et al., 2020). The detection limit, accuracy, and precision for each NMHC were given in (Zhou et al., 2023), following the U.S. Environmental Protection Agency (U.S. EPA) TO-15 method (Agency, 1999). With outliers removed, 834 valid samples were obtained. The analyses for the 60 NMHCs were in good agreement with those analyzed by Prof. Donald Blake's laboratory at the University of California, Irvine (Blake, 2003; Simpson et al., 2010), with goodness-of-fit (R2) values ranging from 0.85-0.97 and slopes ranging from 0.85-1.24. In addition, HCHO was analyzed by high-performance liquid chromatography (Lyu et al., 2020). One calibration standard was run for every ten samples to ensure instrument stability, following a previous study (Cheng et al., 2014).

2. I suggest the author further highlight the problem of overprediction of HCHO since it is very important for ozone formation. Although the VOC is underpredicted, the modeled high HCHO may narrow the real gap between the simulated and observed ozone.

Response: Thanks for the comment. As the most abundant carbonyl compound, HCHO is an important source of radicals and impacts O_3 formation in the troposphere. In this study, Overall, HCHO was biased high and showed urban-rural differences. Generally, uncertainties in emissions of VOCs (particularly, precursors of secondary HCHO,

condensed chemical mechanisms, and meteorological conditions could affect the model performance of HCHO and O_3. We added more discussions on the HCHO simulation in the main text:

1) Lines 31-34 in the revised manuscript:

In terms of different VOC components, alkanes, alkenes, non-naphthalene aromatics (ARO2MN), alkynes and HCHO had prediction-to-observation ratios of 0.53 ± 0.38, 0.51 ± 0.48, 0.31 ± 0.38, 0.41 ± 0.47 and 1.21 ± 1.61, respectively.

2) Lines 380-383 in the revised manuscript:

It is most likely that VOC emissions in CD-U were overpredicted. This could also cause high biases of HCHO, which is mostly generated from secondary production in VOC photochemical reactions (Atkinson and Arey, 2003; Wu et al., 2023).

3) Lines 402-406 in the revised manuscript:

For instance, although the TVOC concentration was well modelled in FS, the simulated ethene (ETHE) accounted for 35% of the alkenes, lower than the observed fraction of over 50%. In addition, the predicted HCHO (3.66 ppbv) was much higher than the observed value (0.42 ppbv).

4) Lines 489-504 in the revised manuscript:

Notably, this study revealed that the model overpredicted HCHO, while some previous studies tend to show underprediction (Luecken et al., 2018; Li et al., 2022b). The biases could result from uncertainties in VOC emissions, chemical mechanisms, model resolution, etc. In general, HCHO is mainly contributed by oxidations of reactive VOCs such as ISOP, ETHE, PRPE, and toluene (TOLU) (Simpson et al., 2010; Wei et al., 2023; Wu et al., 2023). The overprediction of HCHO suggests that there may be excessive emissions of these VOCs or that the reaction rates of some VOCs with OH radicals were overpredicted in the model. Secondly, HCHO predictions could vary by 25−40% with different chemical mechanisms, likely due to differences in hydrogen oxide radicals (HO_x) and VOCs grouping (Knote et al., 2015; Luecken et al., 2018). Lastly, finer model resolution could improve the representation of HCHO, especially at grids where HCHO was substantially affected by point sources (e.g., petrochemical facilities), as has been reported in (Parrish et al., 2012). Considering HCHO is an important source of HO_x radicals and drives ozone production (Wittrock et al., 2006; Li et al., 2021), more investigations are warranted to improve the model performance of HCHO in the future.

5) Lines 541-543 in the revised manuscript:

Alkanes, alkenes, ARO2MN, and alkynes are generally underpredicted, with ratios of 0.53 ± 0.38, 0.51 ± 0.48, 0.31 ± 0.38, and 0.41 ± 0.47, respectively, except for HCHO which is overpredicted, with the ratio of 1.21 ± 1.61.

3. Figure 2 NME and NMB should give the full name.

Response: Thanks for the comment. We added the full name of NMB and NME in Figure 2 (as shown in Figure R1 below).

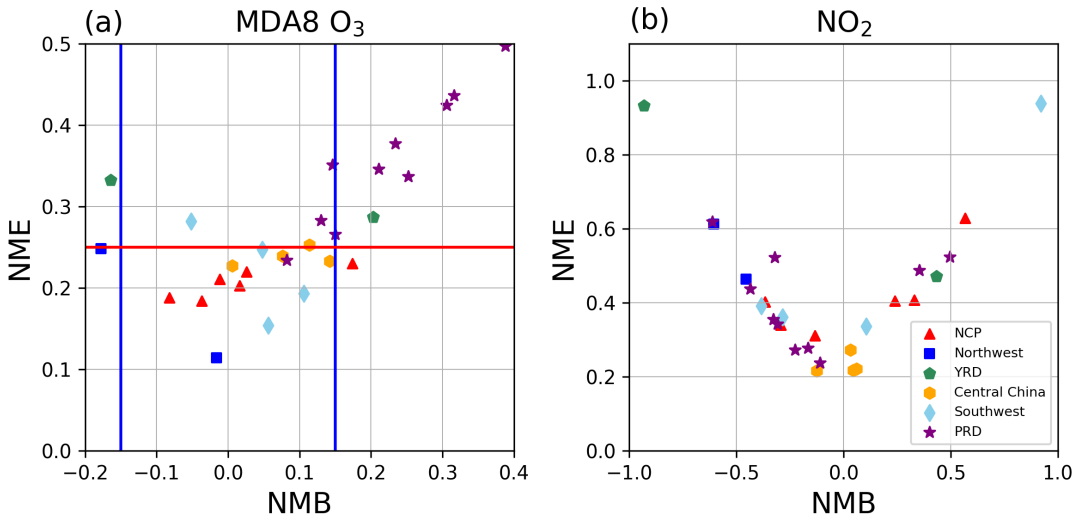

Figure R1. Model performance on MDA8 O_3 and NO_2 at 28 sites in different regions from June 6th to August 24th in 2018. The blue and red lines denote performance criteria (NMB: normalized mean bias, NME: normalized mean error) for MDA8 O_3 suggested by Emery et al. (2017) and the symbols in different colors distinguish different regions of China.

4. Figure 4-6 missed the caption, making it hard for the readers to follow the paper.

Response: Thanks for the comment. We have revised the captions of Figure 4-6 to make them clearer (as shown in Figure R2, R3 and R4 below).

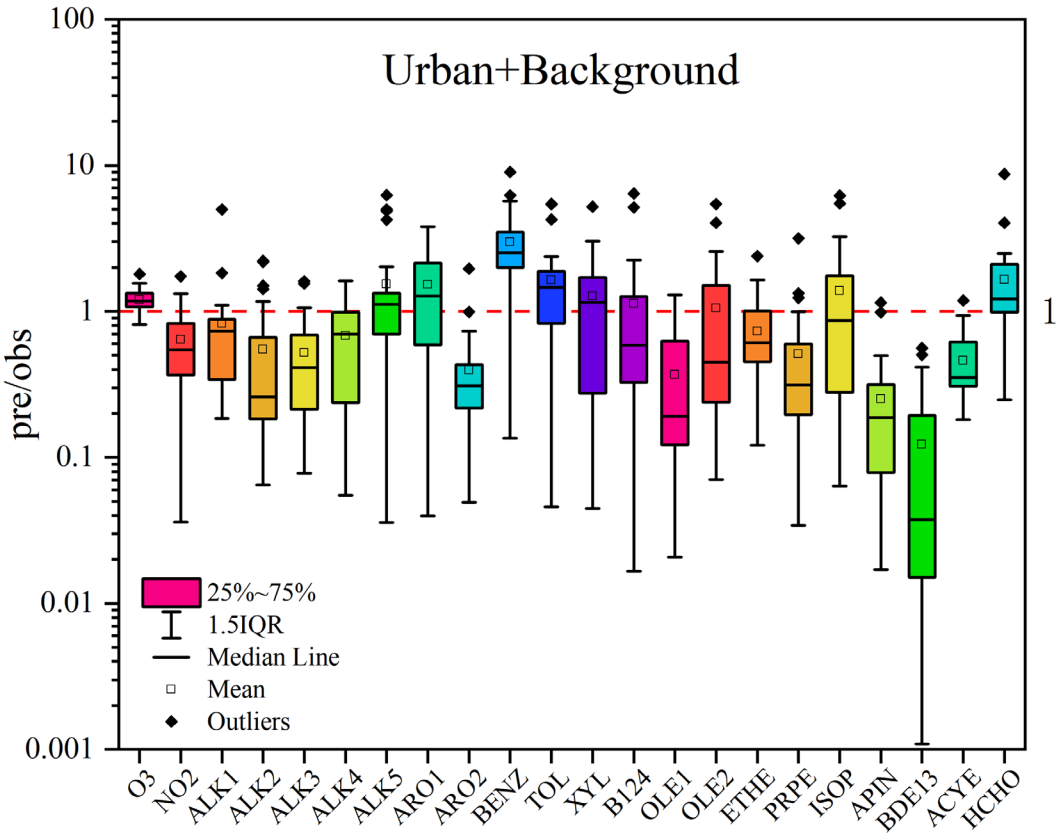

Figure R2. The ratios of prediction-to-observation (pre/obs) for O_3, NO_2 and individual VOCs at 28 sites (including urban and background). The horizontal midlines in boxes represent the median values and the hollow squares depict the mean values. The boxes represent the ratios ranging from the lower and upper quartile for individual VOCs at all sites, and the whiskers represent the 1.5 Interquartile Range (1.5 IQR).

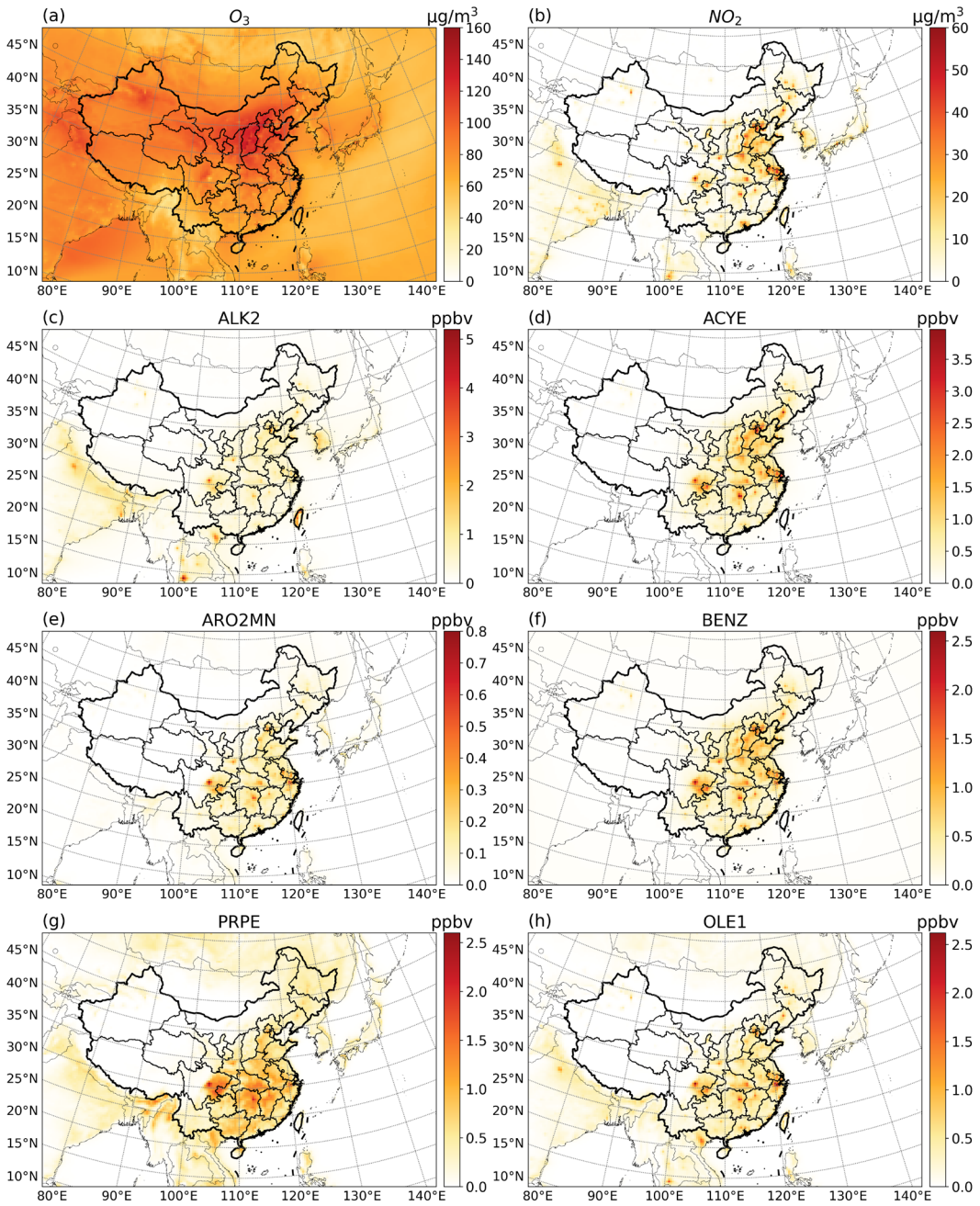

Figure R3. Predicted concentration of (a) O_3, (b) NO_2 and (c-h) six VOCs in the base case from June 6th to August 24th in 2018.

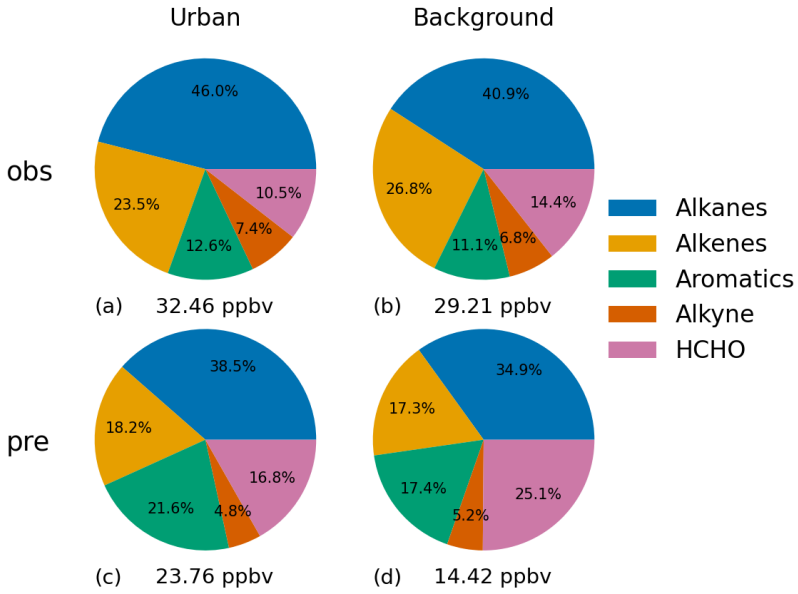

Figure R4. Observed and predicted contributions of different VOCs to the total VOC concentrations at (a and c) urban sites and (b and d) background sites.

5. Figure 3 y-axis ppbv change to concentration (ppbv).

Response: Thanks for the comment. We have revised it as follows.

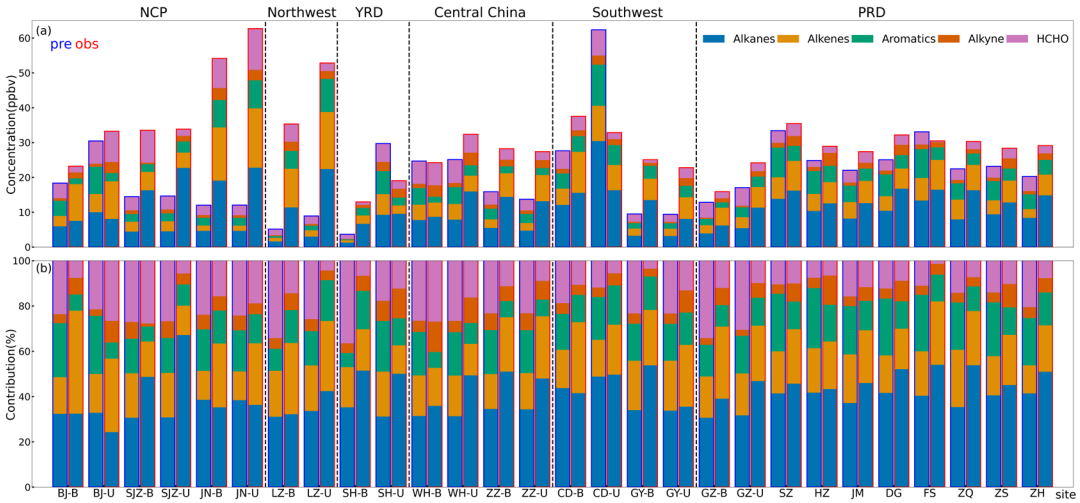

Figure 3. Comparison of predicted and observed VOCs at 28 sites during the study period. (a) The predicted (bars outlined in blue) and observed (bars outlined in red) concentrations at each site; (b) same as (a) but with contributions of VOC groups.

6. Table S1. “Sites in the PRD belong to Urban” change to “Sites in the PRD except GZ belong to Urban”

Response: Thanks, we have made the correction.

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