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 C₂-C₃ 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 O₃ scrubbers installed in front of them to remove airborne O₃. 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).
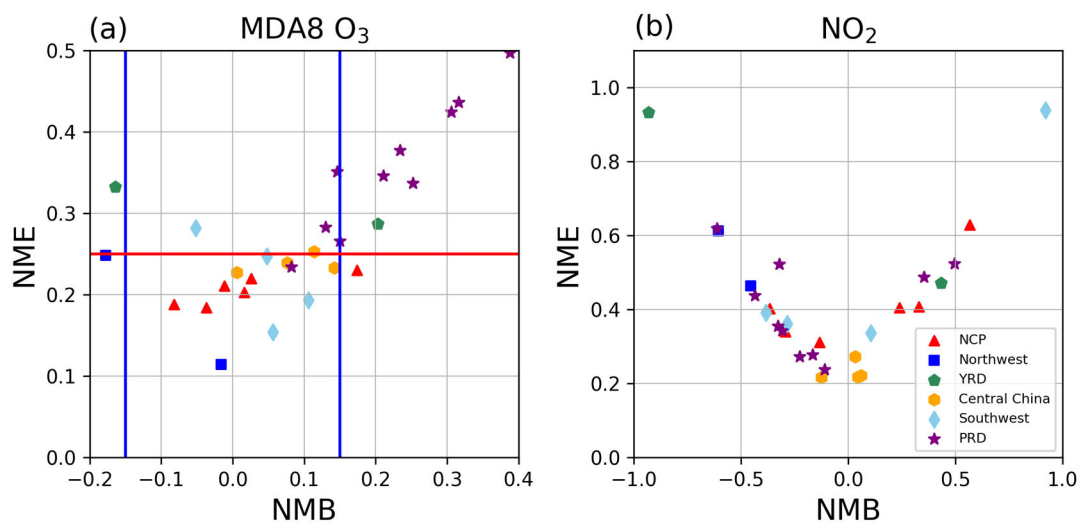

Figure R1. Model performance on MDA8 O_3 and NO_2 at 28 sites in different regions from June 6th to August 24th in 2018. The blue and red lines denote performance criteria (NMB: normalized mean bias, NME: normalized mean error) for MDA8 O_3 suggested by Emery et al. (2017) and the symbols in different 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).
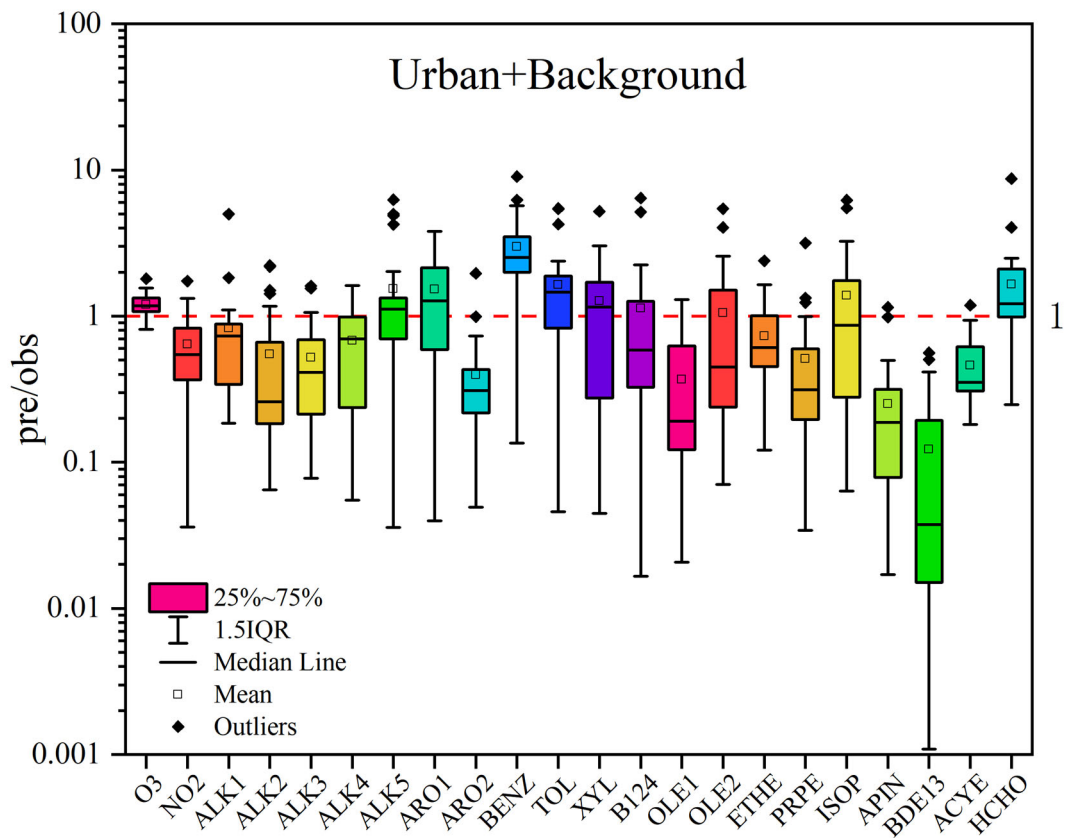
Figure R2. The ratios of prediction-to-observation (pre/obs) for O_3, NO_2 and individual VOCs at 28 sites (including urban and background). The horizontal midlines in boxes represent the median values and the hollow squares depict the mean values. The boxes represent the ratios ranging from the lower and upper quartile for individual VOCs at all sites, and the whiskers represent the 1.5 Interquartile Range (1.5 IQR).
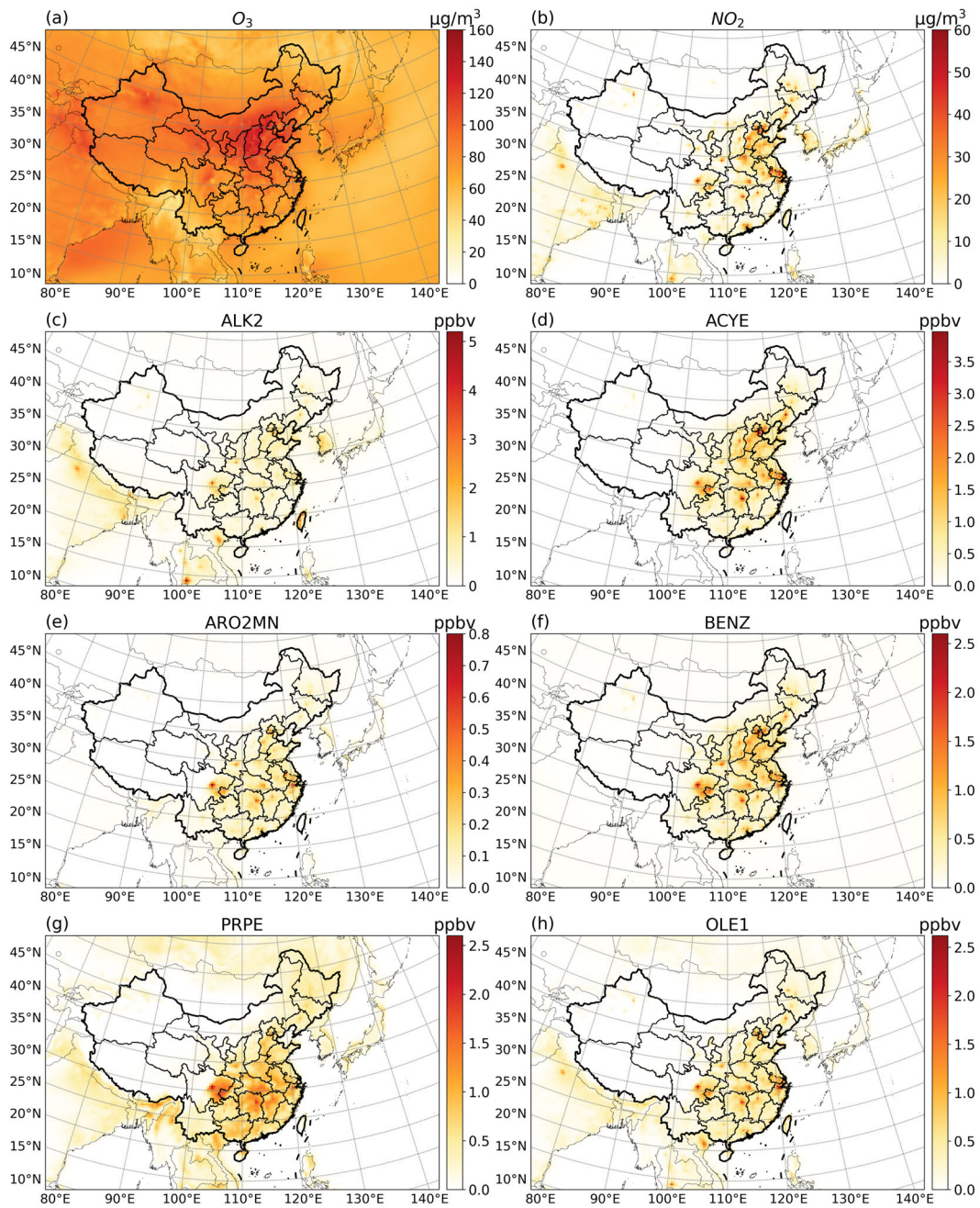
Figure R3. Predicted concentration of (a) O_3, (b) NO_2 and (c-h) six VOCs in the base case from June 6th to August 24th in 2018.
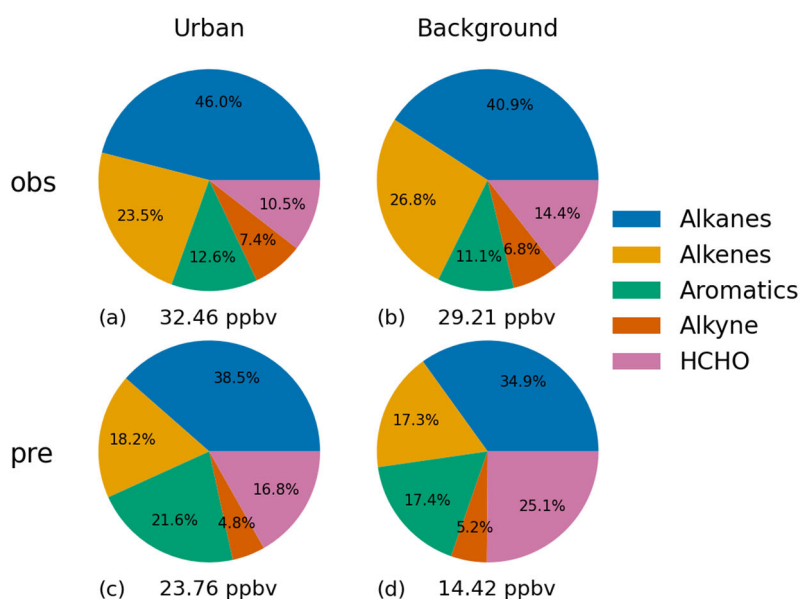
Figure R4. Observed and predicted contributions of different VOCs to the total VOC concentrations at (a and c) urban sites and (b and d) background sites.

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

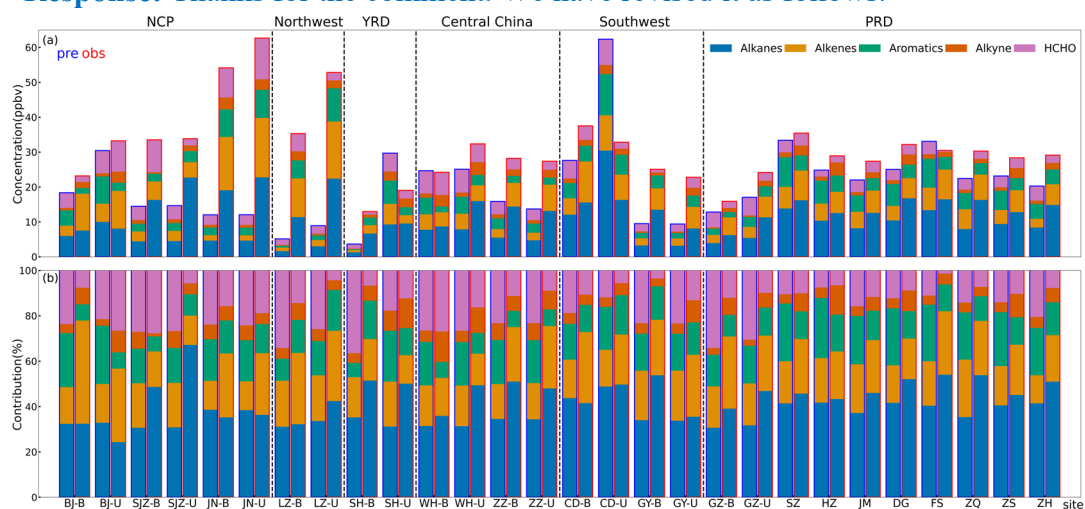**Response:** Thanks for the comment. We have revised it as follows.

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.

Reviewer #2

This manuscript by She et al. evaluated the model performances in simulating volatile organic compounds (VOCs) in summer in multiple cities in China by using the CMAQ model. The author also investigated the influences of adjusting VOC emissions on O_3 simulations and discussed the sensitivities of O_3 to different VOCs. This study enriches our understanding of model performances in simulating VOCs and provides insights for developing VOC emission inventories in the future. The study is logically designed and the manuscript is well organized. I have some editorial suggestions as follows:

Line 70: substantial underprediction of => a substantial underprediction of
Response: Thanks, we have made the correction.

Lines 73-75: "notable effects on air pollutants" vague. What pollutants? "enhance model performance" => "improve model performance".
Response: Thanks for the comment. In the study of Zhu et al. (2019), they analyzed the impact of the augmented VOC emission inventory on O_3 (maximum 8-hr ozone concentrations increase by 17.4 ppb in summer and by 15.6 ppb in winter) and $PM_{2.5}$ (24-hr maximum $PM_{2.5}$ increase by 7.8 $\mu g/m^3$ in winter). We have replaced "air pollutants" with "O_3 and $PM_{2.5}$", and used "improve" instead of "enhance" in the main text.

Line 97: There have been studies evaluating VOC predictions in China so that "for the first time" may not be appropriate. It is recommended to commence a new paragraph from here and add the key findings of this study.
Response: Thanks for the comment. We have removed "for the first time" and revised the paragraph as follows:
Lines 103-109 in the revised manuscript:
The results of this study indicated that the model performance of VOCs in China still has much room to improve, likely with a focus on updating emission inventories in fast-growing industrial cities. Most sites underpredicted TVOCs, and the biases of alkenes significantly impacted O_3 production. These findings enhanced our understanding of the current VOC modelling in air quality models, which could help to improve VOC emission inventory and O_3 prediction in the future.

Lines 100-106: Please rephrase this sentence.
Response: Thanks for the comment. We have rephrased it as follows:
Lines 100-103 in the revised manuscript:
This study aimed to assess the disparities between measured VOC concentrations and predictions in various regions of China using the widely used CMAQ model. We quantified the impacts of VOC biases on O_3 predictions through emission adjustments based on observation-prediction differences.

Line 108: "Observation description" => "Observation data"

Response: Revised.

Line 111: "VOC measurement" => "VOC measurements"
Response: Revised.

Line 113: "collection devices" => "sampling devices"
Response: Revised.

Line 119: "formaldehydes" => "formaldehyde"
Response: Revised.

Line 222: "The observed ratios of TVOCs predictions …" This is confusing. Do you mean "the ratio of observed to predicted TVOCs"?
Response: Thanks for the comment. We have revised it as you suggested.

Lines 239-241: Please rephrase this sentence.
Response: Thanks for the comment. We have rephrased this sentence as follows:
Lines 252-255 in the revised manuscript:
The predicted proportions of aromatics (13.1% to 22.8%) and HCHO (15.3% to 28.9%) were higher than in the observations. In addition, alkynes were predicted to have a minor contribution to TVOCs.

Line 254: Remove "Regarding alkenes".
Response: Revised.

Line 259: "predicted content" => "predicted concentration"
Response: Revised.

Line 260: ACYE was lower than what? "predicted HCHO" => "HCHO"
Response: Thanks for the comment. In this sentence, the predicted ACYE was lower than the observation, we have clarified it in the main text.
Lines 273-275 in the revised manuscript:
Furthermore, the predicted concentration of acetylene (ACYE) was lower than observation at all sites (0.41 ± 0.47 for alkynes), while the HCHO was slightly overpredicted (1.21 ± 1.61 for HCHO).

Line 262: Remove "that" before "the majority of emitted VOCs".
Response: Revised.

Line 313: "concentration differences" => "differences"
Response: Revised.

Line 316: "NO_2 concentrations was" => "NO_2 concentration was"
Response: Revised.

Line 355: "aromatic" => "aromatics"
Response: Revised.

Lines 387-389: Does "ratio" mean the fraction of TVOCs? However, in line 211, "ratio" is specifically referred to as the prediction/observation ratio.
Response: Thanks for the comment. We have made the correction.
Lines 406-408 in the revised manuscript:
The predicted ETHE in ZH was higher (50% of alkenes) than the observation (20% of alkenes), while other cities exhibited similar ETHE percentages.

Line 393: Do you mean "urban and background areas"?
Response: Thanks for the comment. We have made the correction.

Line 403: "with a decrease of 6.91 ppbV compared to the observation values" This is confusing. Are the alkanes underpredicted by 6.91 ppbV?
Response: Thanks for the comment. We clarified in the main text:
Lines 420-422 in the revised manuscript:
Each of the five VOCs showed lower predictions, with alkanes exhibiting the most notable disparity, with a negative bias of 6.91 ppbV compared to the observation values

Line 410: "different regions and urban background areas" => "urban and background areas in different regions"
Response: Revised.

Line 421: "a notable monoterpene" => "an important monoterpene"; "including"=>"originating from"
Response: Revised.

Line 436: "substantial variation" => "a substantial variation"
Response: Revised.

Line 500: "Through considering" => "After considering"; "the MEIC model" => "the MEIC inventory"
Response: Revised.

Line 516: "inaccuracies" => "uncertainties"
Response: Revised.

Thanks for your careful editing to help us improve the English grammar and quality of our manuscript!

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