Responses to the comments of Reviewer #2:

We would like to thank the anonymous referee for his/her comprehensive review and valuable suggestions. These suggestions help us to present our results more clearly. In response, we have made changes according to the referee's suggestions and replied to all comments point by point. All the page and line number for corrections are referred to the revised manuscript, while the page and line number from original reviews are kept intact.

General comments:

As the key precursors of Ozone (O_3), Non-methane volatile organic compounds (NMVOC) have an important influence on the formation of photochemical, secondary organic aerosols and organic acids, harming human health. It is important and challenge to accurate estimate the spatiotemporal distribution of NMVOC emissions. This study presents the NMVOC emissions over China based on EnKF method by assimilating TROPOMI HCHO retrievals. Authors also optimize NOx emissions to reduce the influence of VOC-NOx-O3 chemical feedback. The results showed that the forecast experiment with posterior NMVOC emissions reduced the uncertainty of HCHO and concentrations simulation. And the impact on surface O3 simulation with prior and posterior NMVOC emissions was analyzed. The results will help to improve model forecasts of HCHO, NOx, and O3 concentrations and contribute to design suitable emission reduction policies.

However, the structure of the article should be revised. Authors conducted four set of DA experiments and five set of forecast experiments. They discuss the influence of background error and observation error on the effect of optimizing HCHO emissions. And They also analyzed the impact on surface O3 simulation with prior and posterior NMVOC emissions. Thus, there are too many goals in the study, and it is difficult for readers to remember the setting of these nine experiments. I suggested to delete the discussion about the influence of background error (B) and observation error (R) on the effect of optimizing HCHO emissions in the section 4.4. It would be nice to discuss the influence of the B and R when introducing the EnKF method and explain why authors design the B and R to optimize NMVOC emissions in this study.

Response: We appreciate the reviewer for his/her constructive and up-to-point comments. We have further elaborated on the rationale behind the selection of observational and background error settings. We also briefly discussed the influence of TROPOMI retrieval errors and background errors on optimizing HCHO emissions in Section 2.2 and 2.3, respectively. We also deleted the aforementioned discussion in Section 4.4. Correspondingly, we removed the EMS1, EMS2, and CEP2 experiments from the original manuscript, and renamed the EMS3 experiment to EMS, and renamed the CEP3 experiment to CEP2 in the revised manuscript.

See lines 249-257, pages 8-9.

"Based on validation against a global network of 25 ground-based Fourier transform infrared (FTIR) column measurements (Vigouroux et al., 2020), TROPOMI HCHO overestimates by 25% (<2.5×10^{15} molec cm^{-2}) in clean regions and underestimates by 30% (>=8×10^{15} molec cm^{-2}) in polluted regions. Therefore, we set the measurement error to 30%. To evaluate the effect of observational data retrieval errors on emission estimates, we conducted a sensitivity experiment in which HCHO columns were empirically bias-corrected according to the error characteristics described above (Figure S1). The posterior emissions increased by 12.8% compared to those in the base experiment (EMDA), indicating that the existing retrieval error in HCHO measurements likely exerts an influence on the estimation of NMVOC emissions."

See lines 312-317, page 12.

"… …Based on model evaluation, the uncertainty of NMVOC emissions was set to 40% (Kaiser et al., 2018; Souri et al., 2020; Cao et al., 2018). A sensitivity experiment involving a doubling of the prior uncertainty (80%) revealed that the differences in posterior NMVOC emissions amounted to a mere 0.2% (Figure S2). The implementation of a 'two-step' inversion strategy allows for the timely correction of residual errors from the previous assimilation window in the current window, thus ensuring that the RAPAS system has a relatively low dependence on prior uncertainty settings. This study also addresses uncertainties… …”

See lines 329-347, page 13.

“… …Additionally, we designed a sensitivity experiment (EMS) to illustrate the significance of optimizing NO_x emissions in quantifying VOC-O_3 chemical reactions. In this experiment, NO_x emissions were not optimized. To validate the posterior emissions of NO_x and NMVOCs in EMDA, we compared two parallel forward simulation experiments, denoted as CEP and VEP, corresponding to prior and posterior emission scenarios, respectively, against NO_2 and HCHO measurements. To investigate the impact of optimizing NMVOC emissions on the secondary production and loss of surface O_3, a forward simulation experiment (CEP1) was conducted with the prior NMVOC emissions and the posterior NO_x emissions. Another forward modelling experiment (CEP2) used the posterior emissions of EMS to evaluate its performance.…. …”

See lines 359-360, page 14.

Table 1. The assimilation, sensitivity, and validation experiments conducted in this study.

Exp.Type	Exp. Name	NMVOC emissions	NO_x emissions
Assimilation	EMDA	MEIC 2020 and MEGAN for August (the first DA window), optimized emissions of the previous window (other DA windows)	MEIC 2020 and MEGAN for August (the first DA window), optimized emissions of the previous window (other DA windows)
Sensitivity	EMS	Same as EMDA	MEIC 2020 and MEGAN for August
Validation	CEP	MEIC 2020 and MEGAN for August	MEIC 2020 and MEGAN for August
	VEP	Posterior emissions of EMDA	Posterior emissions of EMDA
	CEP1	Same as CEP	Posterior emissions of EMDA
	CEP2	Posterior emissions of EMS	Same as CEP

Specific comments:

1. Line 40: It should be "Compared with the forecast experiment with prior emission, the forecast with posterior ...". The statement should be revised.

Response: Thank you for your comment. We have changed the statement. See lines 40-41, page 2.

"Compared with the forecast with prior emissions, the forecast with posterior emissions significantly improved HCHO simulations, reducing biases by 75.7%, indicating a notable decrease in posterior emission uncertainties. … …".

2. Line 42: "Moreover" should be deleted. And the statement also should be revised

Response: We have deleted the "Moreover" and enhanced the English expression. See lines 43-45, page 2.

"The forecast with posterior emissions also effectively corrected the overestimation of O_3 in forecast with prior emissions, reducing biases by 49.3%."

3. Line 176: What did you consider about the boundary condition of NMVOC and NOx?

Response: Thank you for this comment. In this study, the boundary conditions for NO_x (including NO and NO_2), O_3, and HCHO were extracted from the outputs of the Whole Atmosphere Community Climate Model (WACCM). For the other components of NMVOCs, since most NMVOC components have a short atmospheric lifetime (Gaubert et al., 2020; Li et al., 2020). For instance, isoprene, which is the primary component of NMVOCs, has a lifetime of approximately 1 h (Bates and Jacob, 2019). Consequently, the chemical lateral boundary conditions for NMVOCs were just derived from background profiles.

We have added relevant descriptions. See lines 178-183, page 6.

"Chemical lateral boundary conditions for NO, NO_2, HCHO, and O_3 were extracted from the output of the global CTM (i.e., the Whole Atmosphere Community Climate Model, WACCM) with a resolution of 0.9° × 1.25° at 6-hour intervals (Marsh et al., 2013). Meanwhile, boundary conditions for the other NMVOCs were obtained directly from background profiles. In the first data assimilation (DA) window, chemical initial conditions (excluding NMVOCs) were also derived from the WACCM outputs, whereas … …”

4. Line 204~207: Did author consider about the correction of NOx and NMVOCs in the DA system?

Response: Yes, NOx and NMVOCs emissions were corrected simultaneously in DA systems. See lines 140-145, page 5.

5. Line 209~210: As NO2 is a kind of short lifetime gas, the concentration of surface NO2 measurements not only present NO2, but also may include NOx. What did you consider about the influence of NO2 observation uncertain on optimizing NOx emissions?

Response: Thank you for this comment. Actually, the perturbed samples of NOx emission in this study are divided to NO_2 and NO with a fixed NO_2/NO ratio of 1/9 (Zhang et al., 2007). The process of NO being oxidized to NO_2 during transport from sources to observation sites is fully taken into account by atmospheric transport models. Therefore, we can directly assimilate NO_2 observations to optimize NOx emissions.

6. Line 265: It would be better to use mosaic diagram to present the data amount of TROPOMI HCHO.

Response: Thank you for your suggestion. We have used mosaic diagram to present the data amount of TROPOMI HCHO. See Figure 1 in the revised manuscript.

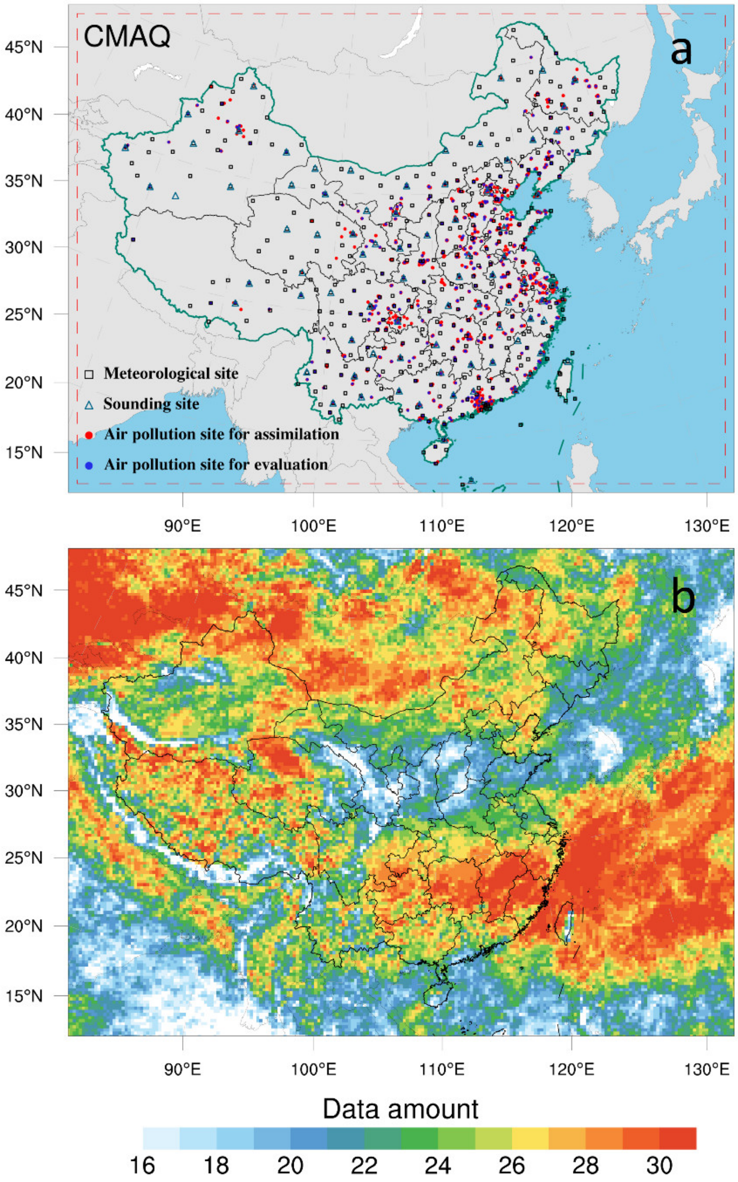

Figure R1. Model domain and observation network (a) and data amount of TROPOMI HCHO retrievals during August 2022 in each grid (b). The red dashed frame delineates the CMAQ computational domain; black squares denote surface meteorological measurement sites; navy triangles indicate sounding sites (Text S1), and red and blue dots represent air pollution measurement sites, where red dots are used for assimilation and blue dots for independent evaluation. (Figure 1 in the revised manuscript)

7. Line 299: Please added the year of the study period.

Response: Thanks. We have added the year of the study period. See line 326, page 12.

"Before implementing the emission inversion, a relatively perfect initial field is generated at 0000 UTC on August 1, 2022 through conducting a 5-day simulation with 6-hour interval 3D-Var data assimilation."

8. Line 307~314: The background error covariance is implicitly expressed in the EnKF method. How did author implement EMS1 experiment in the DA system? And it would be better to introduce EMS1-3 experiment follow the EMDA, making the text description consistent with the Table1.

Response: Thank you for this suggestion. Yes, in the EnKF method, the background error covariance is computed implicitly. However, prior emission uncertainty needs to be provided before implementing the DA system. Specifically, in the EMS1 experiment, we increased the prior uncertainty from 40% to 80%. We have revised this sentence for clarity and precision. See line 313 page 12.

Additionally, we have adjusted the introduction order of those experiments in Section 3, while also removing the EMS1 and EMS2 experiments (See General comments).

"A sensitivity experiment involving a doubling of the prior uncertainty (80%) revealed that the differences in posterior NMVOC emissions… …"

9. Line 324 and 351: "prior and posterior emissions" should be "prior and posterior NMVOC emissions", and "EMGAN" should be "MEGAN".

Response: Corrected. Thanks.

See line 364, page 14.

"Figure 2 shows the spatial distribution of temporally averaged prior and posterior NMVOC emissions, along with … …"

See line 401, page 16.

"**Figure 2.** Spatial distribution of the time-averaged (a) prior emissions (MEIC 2020 + MEGAN), (b) posterior emissions … …"

10. Line 440-441, Figure 5: It is difficult for readers to remember the setting of experiments. And I think that "CEP3" should be "CEP1" in the Fig. 5a?

Response: Thank you for bringing this oversight to our attention. We have corrected the error. Additionally, we have removed the EMS1, EMS2, and CEP2 experiments from the original manuscript (See General comments).

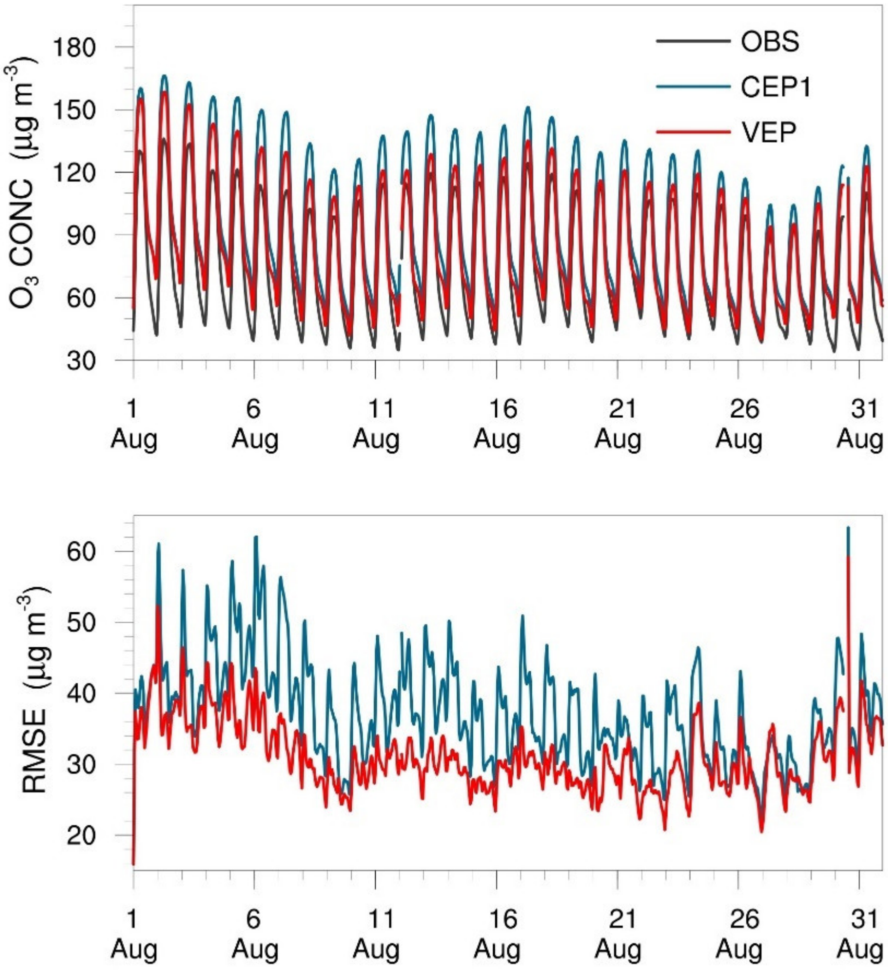

Figure R2. Time series comparison of hourly surface O_3 concentrations (μg m^{-3}) and RMSE (μg m^{-3}) from CEP1 and VEP experiments against all observations. (Figure 5 in the revised manuscript)

11. Line 515-518: The background errors and observation errors play an important role in the DA system. It would be better to give a detailed explanation of why the difference in two posterior NMVOC emissions was small by using ‘two-step’ inversion strategy in the DA system.

Response: Thank you for this suggestion. In this study, we innovatively used a “two-step” optimization strategy, in which the emissions are inferred first and then input into the CMAQ model to simulate initial conditions of the next window. That is, the residual error of the current window is reflected in the initial conditions of the next window. Meanwhile, the optimized emissions are transferred to the next window as prior emissions. Therefore, the residual errors from the current assimilation window will be promptly corrected in the next window. This cyclic iteration inversion ensures that the RAPAS system has a relatively low dependence on prior uncertainty settings (Feng et al., 2023). We have included the following discussion in the revised manuscript.

Lines 158-161, page 6.

“The inversion process follows a two-step procedure within each inversion window, in which the emissions are inferred first and then input into the CMAQ model to simulate initial conditions of the next window. Meanwhile, the optimized emissions are transferred to the next window as prior emissions. The two-step inversion strategy facilitates error propagation and iterative emission optimization, which have… …”

Lines 314-317, page 12.

“A sensitivity experiment involving a doubling of the prior uncertainty (80%) revealed that the differences in posterior NMVOC emissions amounted to a mere 0.2% (Figure S2). The implementation of a ‘two-step’ inversion strategy allows for the timely correction of residual errors from the previous assimilation window in the current window, thus ensuring that the RAPAS system has a relatively low dependence on prior uncertainty settings.”

References

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