Reply to the comments of RC1

RC1: General comment

The revised manuscript, "Spatiotemporal optimization of NO_x and VOC emissions using a hybrid inversion framework and its implication for ozone sensitivity diagnosis" has been significantly improved. The authors have addressed all of the referees' comments and adapted the manuscript, discussion and figures accordingly. I congratulate the authors on their efforts. I now consider the method, analysis, and discussion presented in the manuscript to meet the standards of the ACP journal, and I suggest its publication as soon as the remaining minor points have been addressed.

Response: We sincerely thank the reviewer for the positive assessment and constructive comments. We have addressed all remaining minor points and revised the manuscript accordingly. Below, we provide point-by-point responses. The reviewer's comments are shown in plain text, our responses in **bold**, and revised manuscript text in *italics*.

RC1: Specific comments and responses

Comment 1: Line 26 and 27: Please clarify that you are talking about NO_2 and O_3 concentrations here, not emissions.

Response: We have added the word "concentrations" to clarify that the sentence refers to surface NO_2 and O_3 concentrations, not emissions.

Comment 2: Line 193: Moon (2025) is not listed in the reference list.

Response: We have added Moon (2025) to the reference list.

<Reference in the revised manuscript>

Moon, J.: Inverse Modeling for Constraining Spatiotemporal Distributions of Emissions, PhD thesis, Pusan National University, Busan, South Korea, https://doi.org/10.23172/pusan.000000167548.21016.0000787, 2025.

Comment 3: Line 194: Please remove "paradoxically".

Response: We have deleted the word "paradoxically", as suggested.

Comment 4: Lines 219-233: The authors repeat certain variable definitions many times, which disrupts the reading flow. For example, "i" should only be defined once as "time step" and should not be repeated for all variables with the index "i". Please also adjust " The emission scaling factor ($\alpha_i = e_i/e_i^b$) represents the ratio between the updated and prior emissions at time step i. ei denotes the updated emissions at time step i, and eib denotes the corresponding prior emissions." to " The emission scaling factor ($\alpha_i = e_i/e_i^b$) represents the ratio between the updated emissions (e_i) and the prior emissions (e_i^b)."

Response: We have revised this paragraph to define the time index only once and to describe the control variable more concisely, as suggested. We also revised the description of the emission scaling factor following the reviewer's wording.

<Section 2.3.2 in the revised manuscript>

The emission scaling factor ($\alpha_i = e_i/e_i^b$) represents the ratio between the updated emissions (e_i) and the prior emissions (e_i^b).

Comment 5: Line 303: Is the "hybrid inversion" not the FDMB here?

Response: We apologize for the unclear wording. The phrase "hybrid inversion" in this sentence referred to the final posterior emissions from the full FDMB/4D-Var hybrid inversion, not to the FDMB step alone. To avoid confusion, we have revised the sentence to explicitly state that the adjoint analysis used the posterior emissions from the Hybrid_NOx+VOC experiment.

<Section 2.5 in the revised manuscript>

To this end, a forward CMAQ simulation was first performed using the posterior emissions from the Hybrid_NOx+VOC experiment to generate the concentration fields required for adjoint integration.

Comment 6: Line 330-340: Please revise to avoid repetition of information.

Response: We agree with the reviewer. The original text repeated the description of the receptor hour, emission hour, adjoint simulations, and response calculations. We have shortened this paragraph and moved the detailed explanation to the equations and figure caption where appropriate.

<Section 2.5 in the revised manuscript>

In this configuration, each receptor hour h_r requires a distinct adjoint run; therefore, 24 adjoint simulations were performed for each regime, for a total of 48 runs. Each simulation spanned the full two-week analysis period and simultaneously provided sensitivities to all emission hours h_e. These sensitivities were multiplied by the corresponding posterior emission rates to obtain the emission-time-specific O_3 responses (Eq. 11), and then summed over all emission hours to derive the emission-time-integrated responses (Eq. 12). The overall procedure is summarized in Fig. 4.

Comment 7: Line 344: After the first revision process, "t1" is no longer discussed in the manuscript. Please correct this.

Response: We thank the reviewer for identifying this inconsistency. The notation t_1 was left from an earlier version of the manuscript. We have replaced t_1 with h_e in the Figure 4 caption to maintain consistency with the notation used in the text.

<Caption of Figure 4 in the revised manuscript>

A single adjoint run provides, for a given receptor hour h_r, the sensitivities of the regime-mean surface O_3 diagnostic cost function $\mathcal{J}_{Reg}(h_r)$ to precursor emissions at each emission hour h_e.

Comment 8: Line 492 and 589: Are the MEGAN emissions also not important alongside the EDGAR HTAP emissions, particularly with regard to the biogenic VOCs?

Response: We agree with the reviewer. We revised the text to clarify that, in addition to the EDGAR-HTAPv3 anthropogenic emission uncertainty, MEGAN-derived BVOC emissions may also contribute to uncertainty in HCHO production and HCHO-to-NO_2-based O_3 sensitivity diagnosis, particularly over vegetated and mountainous regions. We also revised the Summary and Conclusions section to state that the Prior experiment used EDGAR-HTAPv3 for anthropogenic emissions and MEGAN v2.1 for biogenic VOC emissions.

<Section 3.3 in the revised manuscript>

This discrepancy in the Prior experiment may partly reflect uncertainties in the prior emission inputs. The prior anthropogenic emissions are based on the 2018 EDGAR-HTAPv3 inventory, whose earlier base year may not fully represent anthropogenic emission conditions in 2022, potentially biasing the Prior experiment toward VOC-sensitive regimes. In addition, BVOC emissions estimated using MEGAN v2.1 may contribute to regime-classification uncertainty, particularly over vegetated and mountainous regions where BVOCs strongly affect HCHO production and thus the HCHO-to-NO_2 ratios. The limited improvement in the Hybrid_NOx experiment further indicates that adjusting NO_x emissions alone is insufficient to capture the observed O_3 sensitivity regimes. These results suggest that simultaneous optimization of both NO_x and VOC emissions is essential for accurately diagnosing O_3 chemical regimes.

<Summary and Conclusions in the revised manuscript>

To assess the impact of major O_3 precursors on the spatiotemporal distribution and sensitivity regime of O_3, three experiments were conducted: Prior, which used EDGAR-HTAPv3 for anthropogenic emissions and MEGAN v2.1 for biogenic VOC emissions; Hybrid_NOx, in which only NO_x emissions were optimized; and Hybrid_NOx+VOC, in which both NO_x and VOC emissions were jointly constrained.

Comment 9: Line 505 and 531: Please add the figure number to the panel descriptions.

Response: We have revised the panel descriptions in the main text to include the figure number.

<*Section 3.4 in the revised manuscript*>

Figures 10a and 10c show the ΔO_3 at each local hour (Korean Standard Time, KST), representing the cumulative response to precursor emissions released across all prior times (Eq. 12).

Figures 10b and 10d focus on 15:00 KST, the hour of maximum O_3 concentration, to illustrate the sensitivity of O_3 at this hour to the timing of precursor emissions.

Comment 10: Line 578: Please elaborate on whether bottom-up approaches are really computationally costly compared to the hybrid inversion approach when considering a full-year analysis.

Response: We have revised the manuscript to clarify that a full-year hybrid inversion would require FDMB and repeated 4D-Var assimilation cycles, and therefore substantial computational resources. Nevertheless, we added that the top-down approach can provide relatively rapid observation-driven emission estimates compared with developing or updating bottom-up inventories based on detailed activity data and source-specific emission factors.

<*Section 3.4 in the revised manuscript*>

Compared with conventional bottom-up inventories, the top-down approach uses atmospheric observations to adjust prior emissions and provide posterior emission estimates that are more consistent with observed concentrations. A full-year hybrid inversion would require FDMB and repeated 4D-Var assimilation cycles and therefore substantial computational resources. However, compared with developing or updating bottom-up inventories based on detailed activity data and source-specific emission factors, the top-down approach can provide relatively rapid observation-driven emission estimates. This approach enables rapid updates of O_3 precursor emissions and provides timely guidance for O_3 management policies.

Comment 11: Line 591-605: Please consider discussing the use of assimilated observations for evaluation again here. For example, improvement of IOA is expected, since the observations are not independent.

Response: We agree with the reviewer. We revised the Summary and Conclusions section to clarify that improvements against AQMS observations used in the inversion should be interpreted as consistency with assimilated observations. We also replaced the previous IOA statement with independent data-splitting validation results, showing that the Hybrid_NOx+VOC experiment reduced the magnitude of O_3 MBE from 3.02 to 0.86 ppb and increased IOA from 0.71 to 0.77 at withheld AQMS sites.

<Summary and Conclusions in the revised manuscript>

In the Hybrid_NOx experiment, where only NO_x emissions were adjusted, emissions decreased by up to 51 % at night and increased by up to 14 % during the day relative to the Prior inventory, resulting in an overall average reduction of 18 %. These time-dependent adjustments enabled the correction of diurnal variability in the emission profile. In the baseline comparison with AQMS observations used in the inversion, nighttime O_3 concentrations increased and the negative O_3 bias was substantially reduced relative to the Prior experiment. In contrast, during the daytime, constraining NO_x emissions alone yielded only limited improvements in O_3 concentrations. This highlights the need for jointly constraining NO_x and VOC emissions to better represent the nonlinear chemical processes controlling daytime O_3 formation.

To address this limitation, the Hybrid_NOx+VOC experiment was conducted, in which both NO_x and VOC emissions were simultaneously constrained. Compared to the Prior emissions, NO_x emissions decreased by an average of 16 %, while anthropogenic AVOC emissions and BVOC emissions increased by 71 % and 162 %, respectively. In the independent data-splitting validation, in which 20 % of AQMS sites were withheld from the inversion, the Hybrid_NOx+VOC experiment reduced the magnitude of O_3 MBE from 3.02 to 0.86 ppb and increased IOA from 0.71 to 0.77 relative to the Prior experiment. These independent validation results support the robustness of the posterior emission corrections and underscore the importance of simultaneously constraining NO_x and VOC emissions and accurately representing their diurnal variability for improving O_3 model performance.