Response to Reviewer 2

We thank the reviewers for the detailed comments and suggestions, also the time and effort that they invested into the review. We believe the revisions have strengthened the manuscript. Below we provide a detailed point-by-point response to all the comments. The reviewers' comments are shown in blue, and our responses follow in black. The changes in the manuscript are highlighted in red and underlined. Page and line numbers are indicated in the revised track-changed version.

General comments

This manuscript presents a comprehensive analysis of ozone (O_3) formation sensitivity across Japan using the secondary formaldehyde-to-nitrogen dioxide ratio (FNRsec), with thresholds derived from GEOS-Chem chemical transport model simulations and sensitivity derived from combination of ground-based observations. The study showed that the vertical and temporal variability of ozone sensitivity is critical for designing effective mitigation strategies.

The main strengths of the manuscript include (1) the novel application of Pandora direct-sun and sky-scan measurements to investigate O_3 sensitivity regimes (2) the explicit separation of secondary and primary HCHO using model-based diagnostics. Overall, the observational–model framework is well designed, and the analysis is detailed.

However, several aspects require clarification or further justification before the conclusions can be fully supported. In particular: (1) the uncertainty and limitations associated with using space-based or column-based FNR indicators to infer PO3 regimes should be discussed (2) the importance of understanding vertical distribution of ozone production sensitivity should be emphasized more clearly in the introduction to better motivate the novelty of the work (3) the reliability of the FNRsec thresholds depends strongly on model performance for HCHO and NO_2, and primary and secondary HCHO separation, which need further discussion.

Overall, the current form of manuscript requires **major revision** before it can be considered suitable for publication. Addressing the scientific and methodological issues outlined below would substantially strengthen the study.

Response:

Thank you very much for the reviewer's comments and suggestions, which have helped us improve the manuscript. We have revised the manuscripts and addressed the current limitations. We have introduced the remaining limitation of FNR indicator compared to more precise indicators such as LROx/LNOx (page 2, lines 64-69).

"The HCHO-to-NO_2 ratio has been proposed as a better indicator because HCHO and NO_2 have similar lifetimes and better represent the competition for OH radicals (Santiago et al., 2021; Tonnesen and Dennis, 2000). The FNR has inherent limitations in representing O_3 chemistry (Souri et al., 2023a). A wide transition/ambiguous range of FNR values has been reported compared with the more precise LNO_x/LRO_x ratio (Schroeder et al., 2017). Consequently, under certain conditions, FNR may misclassify O_3 formation sensitivity. Nonetheless, FNR remains a commonly used indicator because it can be readily obtained and does not require extensive modeling."

The reason why vertical sensitivity should be investigated has been mentioned (page 2, lines 70-78).

"O_3 formation occurs not only at the surface but also at elevated altitudes in the troposphere (Hu et al., 2024). Moreover, due to atmospheric convection, elevated O_3 can be dispersed downward to the near-surface layer (Souri et al., 2021). Indeed, study of O_3 production within the planetary boundary layer (PBL) is more important than at the surface alone. VOCs, such as isoprene emitted from vegetation, can be vertically transported to higher layer, where they produce RO_x radicals and secondarily formed HCHO through photochemical processes. The vertical distributions of HCHO is therefore primarily driven by vertical transport and chemistry, which complicates the vertical formation of tropospheric O_3 (Souri et al., 2023b). To investigate the vertical sensitivity of O_3 formation, previous studies have employed column FNR observed by multi-axis differential optical absorption spectroscopy (MAX-DOAS) (Irie et al., 2021; Zhang et al., 2021; Ryan et al., 2023; Wang et al., 2025)"

We have also mentioned the uncertainty of the FNR threshold derived from the model in Section 3.3 (page 13, lines 563-569).

"For the column, the transition range for Sapporo was defined as 0.86–1.52 where the cumulative probability of NO_x-limited and RO_x-limited condition reached 95 %, corresponding to a 5 % probability of misclassification. Consequently, 15 % of NO_x-limited and 15 % of RO_x-limited conditions were incorrectly classified as transitional (Fig. 7). Similarly, the probabilities of misclassifying NO_x-limited and RO_x-limited conditions as transitional were 20 % and 25 %, respectively, for Tsukuba-NIES, 35 % and 25 % for Tokyo-TMU, and 15 % and 60 % for Fukuoka. Notably, the probability of misclassification of RO_x-limited condition at Fukuoka was higher than at the other locations. Because we simulated for the year 2022, this uncertainty could be reduced by extending the model simulations to longer time periods."

Moreover, due to these limitations of FNR, we have focused the O_3-sensitivity diagnosis during exceedance events using Pandora observations around local noon to maximize the accuracy.

Specific comments:

1. **Consistency between FNRsec thresholds and observational application.**

It is somewhat confusing that the FNRsec thresholds are derived from GEOS-Chem perturbation simulations using secondary HCHO, but the ratios for in-situ and Pandora observations are total HCHO/NO_2 (hereafter FNR_all). Applying the thresholds to the observations to diagnose the PO3 sensitivity, which means comparing FNR_all with FNRsec-based thresholds, may introduce systematic bias, as lower thresholds would tend to classify more conditions as NOx-limited.

The authors should clarify how this inconsistency is addressed. It would be helpful to add a separate section in which the FNRsec thresholds are first applied to GEOS-Chem–derived FNRsec, producing regime diagnostics analogous to Fig. 8, and then compare those results with the regime classification obtained using Pandora-derived FNR_all. This comparison would allow readers to better assess the implications of applying FNRsec thresholds to observational data.

In addition, the thresholds are currently derived using data aggregated over the entire year. Given that ozone production efficiency is much lower during cold seasons, the authors may consider focusing threshold derivation on the warmer months, when photochemical ozone production is most relevant, and focus the analysis on the warm season as well.

Response:

The authors would like to clarify the FNR_{sec} threshold derived from GEOS-Chem simulations and how it was applied to in-situ and Pandora measurements. First, we separated the temporal and spatial distributions of secondary HCHO in the atmosphere using the GEOS-Chem model (Section 3.1.2). In the next step, these distributions were adopted for both in situ and Pandora measurements to identify surface, column, and vertical profile of secondary HCHO. The FNR_{sec} values for in-situ and Pandora observations were then determined using the secondary HCHO.

During summer, we found that the O_3 sensitivity regime was primarily NO_x-limited; therefore, the cumulative probability of radical-limited conditions could not be obtained in Figure 7.
Following the reviewers' suggestions, we restricted the diagnostics during O_3 exceedance events to Pandora observations around noon. This will help to minimize the uncertainty of FNR for interpreting O_3 productions.

2. Assumptions in separating secondary HCHO

The approach of turning off anthropogenic HCHO emissions to isolate secondary HCHO is reasonable. However, it implicitly assumes that the chemical processes controlling secondary HCHO formation are not significantly altered by the removal of primary HCHO sources. The authors should clarify whether and how this assumption holds, and discuss potential biases introduced by this approach. A sensitivity discussion with reference to studies that explicitly validate this methodology would strengthen confidence in the derived FNRsec.

Response:

Primary HCHO affects O_3 production by acting as a VOC and generating HO_2 and OH radicals (Lei et al., 2009). However, even under conditions with a high primary HCHO contribution (> 58 %), its impact has been reported to enhance HO_2 radical by 11 %, OH radical by 5 %, and O_3 concentrations by 6 % (Lei et al., 2009).
At our study locations, the contribution of primary HCHO to column HCHO was within 10%. Therefore, the impact of turning off anthropogenic HCHO emissions was minimal.

3. Interpretation of "external transport" removal

In Sect. 2.3, the manuscript states that external transport is "eliminated" by subtracting Run-3 or Run-4 from Run-2. This description is potentially misleading, as emission perturbation experiments do not strictly isolate transport processes. The authors should clarify a. which component of transport or background influence is being minimized by this subtraction, and b. how the resulting VOC and NOx emission reductions should be interpreted physically.

Response:

We mean the external O_3 concentrations were eliminated by this subtraction. We perturbated only Japan nationwide emissions (Run-3 and Run-4). The O_3 productions in other regions and long-range transports were similar for Run-3 or Run-4 compared to Run-2. Therefore, the subtraction eliminated long-range transport of O_3 leading to more precisely in investigating of the internal O_3 production.

4. Representativeness of in-situ surface measurements

Surface in-situ measurement is only available at Tokyo-TMU and only for limited periods (July and October 2022). Comparisons with surface HCHO/NO2 derived from Pandora observations could help extent the surface regime diagnose.

Response:

We would like to thank the reviewer for the suggestion. However, Pandora surface products have not yet been well validated; therefore, the use of surface $HCHO/NO_2$ derived from Pandora observations could introduce substantial uncertainty into the FNR values.
Pandora surface concentrations represent the lowest retrieval layer in the MAXDOAS profile products. Since the Pandora instruments at the study locations are typically installed at 50 m above sea level (135 m at the Tokyo-TMU), the reported surface concentrations correspond to the layer centered at these altitudes rather than the actual ground surface.

5. Policy relevance

The discussion of policy implications in the Conclusions is useful but remains somewhat general. The authors may consider adding a brief, concrete example to more directly connect the scientific findings with actionable air quality management strategies for Japan, particularly given the regional focus of the study.

Response:

Following the recommendations of the two reviewers, we have revised the manuscript to focus the analysis on high O_3 episodes using Pandora observations around local noon (Section 3.4). The management strategies are suggested accordingly for these events in the revised version.

For Sapporo (page 15, lines 620-623):

"At Sapporo, the O_3 concentrations increased during spring (Fig. 8). All eight events with MDA8 O_3 exceeding 60 ppbv occurred in April and May 2022. Pandora observations were unavailable on 21 and 22 May 2022. Given the transition range determined at Sapporo (0.86 < FNR_{sec} <1.52), the column FNR_{sec} exhibited O_3 sensitivity in transitional and NO_x-limited regime. Therefore, reducing NO_x emission would be the optimal strategy for mitigating O_3 levels."

For Tsukuba-NIES (page 16, lines 639-646):

"Compare with Sapporo, more O_3 exceedance events were found at Tsukuba-NIES, with 30 events in 2022. These events primarily took place during spring and summer. Like the results at Sapporo, the column FNR_{sec} exhibited transitional and NO_x-limited conditions during spring events, whereas O_3 chemistry was almost entirely NO_x-limited during summer events, likely due to substantial enhancement in HCHO production (Fig. S11). Regarding vertical sensitivity, we determined a lower probability of RO_x-limited regime during the spring events. During summer events, O_3 formation sensitivity throughout the lower troposphere was consistently NO_x-limited, consistent with the column FNR_{sec} classification. Thus, emission policies focusing on continued reductions in NO_x would effectively improve tropospheric O_3 pollution during summer."

For Tokyo-TMU and Fukuoka (page 17, lines 660-666):

"The exceedance events of O_3 spanned a broad period from spring through fall at both Tokyo-TMU and Fukuoka (Figs. 10 and 11). The column FNR_{sec} were higher during summer leading to a dominant classification in the NO_x-limited regime. Transitional conditions were observed more frequently during spring and fall. At Tokyo-TMU, only one exceedance event (7 April) was found to be sensitive to RO_x radicals. The locally elevated NO_x emissions on that event shifted the chemical environment downward to lower FNR_{sec} values (Fig. S12). Vertical sensitivity profiles showed a RO_x-limited regime within the lower 1 km on 7-8 April. For Fukuoka, the transitional condition occurred more frequently during the exceedance events, emphasizing the need for simultaneous control strategies targeting both NO_x and VOCs in this region."

Technical corrections

Consider adding a separate paragraph in the Introduction explicitly describing the motivation and importance of studying the vertical distribution of ozone sensitivity regimes within the troposphere.

Response:

We have modified the Introduction to provide a description on vertical distribution of O_3 sensitivity regime (page 2, lines 70-78).

"O_3 formation occurs not only at the surface but also at elevated altitudes in the troposphere (Hu et al., 2024). Moreover, due to atmospheric convection, elevated O_3 can be dispersed downward to the near-surface layer (Souri et al., 2021). Indeed, study of O_3 production within the planetary boundary layer (PBL) is more sufficient than at the surface alone. VOCs, such as isoprene emitted from vegetation, can be vertically transported to higher layer, where they produce RO_x radicals and secondarily formed HCHO through photochemical processes. The vertical distributions of HCHO is therefore primarily driven by vertical transport and chemistry, which complicates the vertical formation of tropospheric O_3 (Souri et al., 2023b). To investigate the vertical sensitivity of O_3 formation, previous studies have employed column FNR observed by multi-axis differential optical absorption spectroscopy (MAX-DOAS) (Irie et al., 2021; Zhang et al., 2021; Ryan et al., 2023; Wang et al., 2025)."

Sections 3.1 and 3.2 could potentially be combined, as both primarily describe diurnal and seasonal patterns of HCHO and NO_2. In addition, it would be useful to explicitly present the temporal evolution of FNR values themselves, since these are directly compared with thresholds to diagnose regimes.

Response:

Because Sections 3.1 and 3.2 are relatively long, we would like to keep them as separate sections in the main text.
To minimize uncertainty in column FNR, according to the reviewer #1's comments, we revised the manuscript to present only column FNR values using Pandora observations around noon (12:00 ± 2:00).

To maintain consistency with the main results, the abstract should briefly mention the diurnal variation of ozone sensitivity regimes. Currently, only seasonality and vertical variations are mentioned.

Response:

As suggested by reviewers, we focused the analysis on Pandora observations around noon the maximize accuracy. The abstract was modified relevantly, and removed diurnal, seasonal variation of O_3 formation sensitivity.

Several instances of "nitrogen_dioxide" appear in the text; this should be consistently formatted as "nitrogen dioxide" or "NO_2."

Response:

We have revised "nitrogen_dioxide" to the correct term "nitrogen dioxide".

Line 80: consider revising "extensive studies on O_3 formation are needed to efficiently mitigate human exposure" to "... needed to more efficiently mitigate human exposure," to reflect improvement relative to current mitigation effectiveness.

Response:

We have revised the sentence (page 3, lines 114-115).
"Therefore, extensive studies on O_3 formation are needed to more efficiently mitigate human exposure."

References

Hu, Q., Ji, X., Hong, Q., Li, J., Li, Q., Ou, J., Liu, H., Xing, C., Tan, W., Chen, J., Chang, B., and Liu, C.: Vertical Evolution of Ozone Formation Sensitivity Based on Synchronous Vertical Observations of Ozone and Proxies for Its Precursors: Implications for Ozone Pollution Prevention Strategies, Environ. Sci. Technol., acs.est.4c00637, https://doi.org/10.1021/acs.est.4c00637, 2024.

Irie, H., Yonekawa, D., Damiani, A., Hoque, H. M. S., Sudo, K., and Itahashi, S.: Continuous multi-component MAX-DOAS observations for the planetary boundary layer ozone variation analysis at Chiba and Tsukuba, Japan, from 2013 to 2019, Prog. Earth Planet. Sci., 8, 31, https://doi.org/10.1186/s40645-021-00424-9, 2021.

Lei, W., Zavala, M., De Foy, B., Volkamer, R., Molina, M. J., and Molina, L. T.: Impact of primary formaldehyde on air pollution in the Mexico City Metropolitan Area, Atmos. Chem. Phys., 9, 2607–2618, https://doi.org/10.5194/acp-9-2607-2009, 2009.

Ryan, R. G., Marais, E. A., Gershenson-Smith, E., Ramsay, R., Muller, J.-P., Tirpitz, J.-L., and Frieß, U.: Measurement report: MAX-DOAS measurements characterise Central London ozone pollution episodes during 2022 heatwaves, Atmos. Chem. Phys., 23, 7121–7139, https://doi.org/10.5194/acp-23-7121-2023, 2023.

Santiago, J. V., Inoue, K., and Tonokura, K.: Diagnosis of ozone formation sensitivity in the Mexico City Metropolitan Area using HCHO/NO2 column ratios from the ozone monitoring instrument, Environ. Adv., 6, 100138, https://doi.org/https://doi.org/10.1016/j.envadv.2021.100138, 2021.

Schroeder, J. R., Crawford, J. H., Fried, A., Walega, J., Weinheimer, A., Wisthaler, A., Müller, M., Mikoviny, T., Chen, G., Shook, M., Blake, D. R., and Tonnesen, G. S.: New insights into the column CH_2 O/NO_2 ratio as an indicator of near-surface ozone sensitivity, JGR Atmospheres, 122, 8885–8907, https://doi.org/10.1002/2017JD026781, 2017.

Souri, A. H., Chance, K., Bak, J., Nowlan, C. R., González Abad, G., Jung, Y., Wong, D. C., Mao, J., and Liu, X.: Unraveling pathways of elevated ozone induced by the 2020 lockdown in Europe by an observationally constrained regional model using TROPOMI, Atmos. Chem. Phys., 21, 18227–18245, https://doi.org/10.5194/acp-21-18227-2021, 2021.

Souri, A. H., Johnson, M. S., Wolfe, G. M., Crawford, J. H., Fried, A., Wisthaler, A., Brune, W. H., Blake, D. R., Weinheimer, A. J., Verhoelst, T., Compernolle, S., Pinardi, G., Vigouroux, C., Langerock, B., Choi, S., Lamsal, L., Zhu, L., Sun, S., Cohen, R. C., et al.: Characterization of errors in satellite-based $HCHO/NO_2$ tropospheric column ratios with respect to chemistry, column-to-PBL translation, spatial representation, and retrieval uncertainties, Atmos. Chem. Phys., 23, 1963–1986, https://doi.org/10.5194/acp-23-1963-2023, 2023a.

Souri, A. H., Kumar, R., Chong, H., Golbazi, M., Knowland, K. E., Geddes, J., and Johnson, M. S.: Decoupling in the vertical shape of HCHO during a sea breeze event: The effect on trace gas satellite retrievals and column-to-surface translation, Atmos. Environ., 309, 119929, https://doi.org/10.1016/j.atmosenv.2023.119929, 2023b.

Tonnesen, G. S. and Dennis, R. L.: Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and NO_x: 2. Long-lived species as indicators of ozone concentration sensitivity, J. Geophys. Res. Atmos., 105, 9227–9241, https://doi.org/10.1029/1999jd900372, 2000.

Wang, Z., Zhang, H., Shi, C., Ji, X., Zhu, Y., Xia, C., Sun, X., Zhang, M., Lin, X., Yan, S., Zhou, Y., Xing, C., Chen, Y., and Liu, C.: Vertical and spatial differences in ozone formation sensitivities under different ozone pollution levels in eastern Chinese cities, npj Clim Atmos Sci, 8, 30, https://doi.org/10.1038/s41612-024-00855-3, 2025.

Zhang, S., Wang, S., Zhang, R., Guo, Y., Yan, Y., Ding, Z., and Zhou, B.: Investigating the Sources of Formaldehyde and Corresponding Photochemical Indications at a Suburb Site in

Shanghai From MAX-DOAS Measurements, J. Geophys. Res. Atmos., 126, e2020JD033351, https://doi.org/10.1029/2020JD033351, 2021.