

Reply to Anonymous Referee #1

We thank the reviewer for the careful reading of the manuscript and helpful comments. We have revised the manuscript following the suggestion, as described below.

Wang et al. investigate the monthly and spatial variability of ozone (O_3) formation in the Guanzhong Basin and discuss implications for mitigating O_3 and secondary aerosol pollution. The study combines in situ observations with WRF-Chem simulations and includes analyses of EKMA regimes and source contributions. Overall, the approach is sound and the analyses are carefully conducted. I recommend minor revision before publication.

1. My first comment is about the application of EKMA isopleth profiles to MDA8 O_3 . EKMA analyses are most commonly applied to O_3 production rates, with the goal of quantifying the sensitivity of local photochemical O_3 production to local NO_x and VOC emissions. In this study, EKMA is applied directly to MDA8 O_3 , which includes not only local chemical production but also the effects of transport and advection. It would be helpful for the authors to discuss the extent to which transport and advection may influence the EKMA results, and to clarify why this approach is appropriate for MDA8 O_3 in the present context.

Response: We thank the reviewer for this insightful comment. We agree that EKMA is originally devised in the context of O_3 production and that MDA8 O_3 might include contributions from transport. We have added explanations in Section 2.3 and discussions in Section 3.3 of the revised manuscript as follows,

L98-104: *“The high-resolution, online-coupled WRF-Chem framework simulates all key processes affecting O_3 formation (local photochemistry, regional transport, vertical mixing) consistently. By varying emissions under fixed meteorology and boundary conditions, the model isolates the net impact of emission changes on MDA8 O_3 concentrations. While the classical EKMA method based on O_3 production rates reflects a more localized chemical mechanism, our approach provides an integrated,*

policy-relevant sensitivity diagnosis that accounts for both formation and transport at the urban-regional scale, offering directly actionable insight for control strategies (Ye et al., 2025).”

L107-113: *“In the present study, MDA8 O₃ concentrations are used as the response metric in chemical regime identification and source apportionment for several key reasons. First, MDA8 O₃ represents the period of highest daily O₃ exposure, offering a robust indicator of actual O₃ pollution levels. Second, it is the official metric for ambient O₃ standards under China’s national air quality regulations. Assessing how MDA8 O₃ responds to emission perturbations therefore provides direct, policy-relevant insights for designing effective air quality management and control strategies.”*

L258-276: *“It is important to recognize that MDA8 O₃ variations in the EKMA diagrams integrate contributions from both local photochemical production and atmospheric transport and advection. Multiple recent modeling studies demonstrate that transport processes can contribute substantially to the regional O₃ burden. For example, concentration and mass budget analyses show that horizontal advection from upwind regions and entrainment from the residual layer can supply a significant portion of O₃ mass to a receptor region, especially during morning hours or under synoptic transport conditions, even if local photochemistry subsequently drives the daytime increase in surface O₃ (Qu et al., 2023). In the study, the design of EKMA simulations isolates the chemical sensitivity to precursor emissions by holding the meteorological fields and chemical boundary conditions fixed across all scenarios. Because circulation and transport are invariant in this framework, changes in MDA8 O₃ arising from systematic reductions in NO_x and VOCs emissions mainly reflect the in-situ chemical response of O₃ formation rather than changes in transport dynamics.*

It is worth noting that transport and advection represent a background forcing for region O₃ concentrations. Studies of tropospheric O₃ and its precursors emphasize that long-range transport of O₃ and its precursors can influence surface O₃ trends and variability, and that such transport sets the baseline on which local chemistry operates

(Han et al., 2019; Garatachea et al., 2024; Chen et al., 2025). These transport influences can bias the placement of EKMA isolines in cases where background precursor concentrations (e.g., high transported NO_x or VOCs) differ substantially from typical values, potentially shifting the diagnosed sensitivity toward VOCs-limited or NO_x-limited regimes under certain conditions (Elshorbany et al., 2024). In this study, to mitigate the influence of transport and advection on EKMA results, we select representative O₃ pollution days that exclude anomalous episodes with unusually high backgrounds of transported O₃ and its precursor, such as strong synoptic advection or intrusion events. Hence, the EKMA diagnostics primarily capture the local chemical response to precursor perturbations under typical regional circulation patterns.”

Reference:

Chen, C., Chen, W., Guo, L., Wu, Y., Duan, X., Wang, X., and Shao, M.: A comprehensive review of tropospheric background ozone: definitions, estimation methods, and meta-analysis of its spatiotemporal distribution in China, *Atmos. Chem. Phys.*, 25, 15145–15169, doi:10.5194/acp-25-15145-2025, 2025.

Elshorbany, Y., Ziemke, J. R., Strode, S., Petetin, H., Miyazaki, K., De Smedt, I., Pickering, K., Seguel, R. J., Worden, H., Emmerichs, T., Taraborrelli, D., Cazorla, M., Fadnavis, S., Buchholz, R. R., Gaubert, B., Rojas, N. Y., Nogueira, T., Salameh, T., and Huang, M.: Tropospheric ozone precursors: global and regional distributions, trends, and variability, *Atmos. Chem. Phys.*, 24, 12225–12257, doi:10.5194/acp-24-12225-2024, 2024.

Garatachea, R., Pay, M. T., Achebak, H., Jorba, O., Bowdalo, D., Guevara, M., Petetin, H., Ballester, J., and Pérez García-Pando, C.: National and transboundary contributions to surface ozone concentration across European countries, *Commun. Earth Environ.*, 5, 588, doi:10.1038/s43247-024-01716-w, 2024.

Han, H., Liu, J., Yuan, H., Wang, T., Zhuang, B., and Zhang, X.: Foreign influences on tropospheric ozone over East Asia through global atmospheric transport, *Atmos. Chem. Phys.*, 19, 12495–12514, doi:10.5194/acp-19-12495-2019, 2019.

Qu, K., Wang, X., Cai, X., Yan, Y., Jin, X., Vrekoussis, M., Kanakidou, M., Brasseur, G. P., Shen, J., Xiao, T., Zeng, L., & Zhang, Y. Rethinking the role of transport and photochemistry in regional ozone pollution: Insights from ozone concentration and mass budgets. *Atmos. Chem. Phys.*, 7653–7671. <https://doi.org/10.5194/acp-23-7653-2023>, 2023.

2. My second comment relates to the source attribution methodology. It is unclear whether the O₃ attributed to individual source sectors is calculated by completely removing the corresponding emission source and comparing against the base case, or by incrementally reducing emissions. Additional discussion of how chemical nonlinearity in O₃ formation may affect the source attribution would strengthen this part of the analysis.

Response: We appreciate the reviewer's query regarding the source attribution details. In the BFM application, we have completely removed one sector at a time (industry, power, traffic, residential, biogenic) in separate sensitivity simulations, and compared the resulting MDA8 O₃ and SA concentrations against the base case. We have clarified in Section 2.3 as follows,

L105-107: *“The BFM calculates the contribution of a specific source sector by completely removing (setting to zero) all emissions from that sector in the base simulation and comparing the resulting MDA8 O₃/SA concentration with the base case (Dunker et al., 1996).”*

We fully agree with the reviewer that chemical nonlinearity is a critical consideration. To address this, we have added a new paragraph in Section 3.4 discussing this limitation.

L321-336: *“The source contributions presented in this study are quantified using the BFM, wherein emissions from a specific sector are entirely removed to evaluate its potential impact on O₃ concentrations. While this approach is effective for assessing the control potential of individual sources and is widely used in policy-relevant scenario analysis, it is important to consider the inherent nonlinearity of tropospheric O₃ chemistry. The response of O₃ concentrations to a given emission change depends strongly on the background chemical regime (NO_x- vs. VOCs-limited, as shown in Section 3.3). For example, in a VOCs-limited regime, reducing NO_x emissions alone may inadvertently increase O₃ concentrations, whereas the same reduction in a NO_x-limited regime would lower O₃ concentrations. Consequently, the attribution*

derived from complete removal of a source may not scale linearly with incremental emission controls. As discussed in Li et al. (2023), when emission perturbations are large, the assumption of a linear response between emission change and O₃ change becomes invalid due to the nonlinear interactions in O₃ production chemistry, meaning that attribution results from BFM may differ from those obtained by alternative methods such as source tagging that explicitly follow chemical pathways. Importantly, BFM and tagging methods answer different scientific questions that the BFM estimates the sensitivity of O₃ to sector-specific emission changes, whereas tagging method attributes the total mass of O₃ to source precursors independent of changes in emissions (Li et al., 2023; Shu et al., 2023). In this study, the BFM results are interpreted in conjunction with the OFR analysis (Section 3.3), which delineates the nonlinear photochemical sensitivity to gradual precursor changes. Together, they provide a robust basis for identifying priority source sectors and designing effective, regime-specific control strategies for the GZB.”

Reference:

Li, P., Yang, Y., Wang, H., Su, L., Li, S., et al.: Source attribution of near-surface ozone trends in the United States during 1995–2019, Atmos. Chem. Phys., 23, 5403–5417, doi:10.5194/acp-23-5403-2023, 2023.

Shu, Q., Napelenok, S. L., Hutzell, W. T., Baker, K. R., Henderson, B. H., Murphy, B. N., and Hogrefe, C.: Comparison of ozone formation attribution techniques in the northeastern United States, Geosci. Model Dev., 16, 2303–2322, doi:10.5194/gmd-16-2303-2023, 2023.

3. Finally, the structure of the Results section, particularly Section 3.3, could be improved for clarity. While the descriptions of individual figures are thorough, the section is quite dense. In particular, a clearer separation of the roles of local meteorology (largely uncontrollable) versus emissions (policy-relevant factors) across different cities and months would help readers better follow the key messages.

Response: We thank the reviewer for the constructive suggestion to improve the clarity

of the Results section. We have thoroughly revised Section 3.3 by dividing it into subsections to better separate the roles of meteorological drivers and emission-related factors. The revised sections are as follows,

L173-276: “3.3 Spatiotemporal Patterns of O₃ Sensitivity from EKMA Analysis

O₃ formation in the planetary boundary layer (PBL) is a complex and nonlinear process driven by sunlight acting on NO_x and VOCs. Figures 3 and 4 present EKMA diagrams for four high-O₃ pollution episodes from May to August 2022 in urban areas of the GZB and its five cities, respectively. These diagrams depict O₃ isopleths for OFR identification, derived from sensitivity simulations with systematically reduced NO_x and AVOCs emissions. The ridge line (red lines) delineates the boundary between these regimes: scenarios above it lie in the VOCs-limited regime (O₃ falls more with AVOCs cut), those below in the NO_x-limited regimes, and scenarios near the line are transitional regimes (mixed sensitivity). The upper-right corner (100% AVOCs, 100% NO_x emissions) represents the current emission scenario, whose location relative to the ridge line determines the prevailing sensitivity regime.

3.3.1 Spatiotemporal Shifts in OFR

EKMA curves reveal a pronounced sub-seasonal progression of OFR across the GZB. In May and June, the basin as a whole is predominantly VOCs-limited, indicating AVOCs reductions would substantially lower O₃ concentrations, whereas moderate NO_x cuts could exacerbate O₃ pollution (Figs. 3a, 3b). By July, OFR in urban areas shifts toward a transitional regime (Fig. 3c). In August, the GZB enters a NO_x-limited regime (Fig. 3d), where a 40% NO_x reduction yields an 11.1% decrease in MDA8 O₃, compared to only 3% for an equal AVOCs cut. City-scale analyses show marked spatial heterogeneity (Fig. 4). In early summer, XA, XY, WN, and TC exhibit VOCs-limited regimes. BJ generally falls within NO_x-limited or transitional regimes. WN is the most NO_x-saturated (VOCs-limited) city. By August, OFRs in all cities except WN (transitional) become NO_x-limited.

To assess the robustness of the simulated sub-seasonal OFR progression against

interannual variability in meteorology and emissions, we further examine the formaldehyde-to-NO₂ ratio (FNR) from satellite retrievals for the GZB region over three consecutive warm seasons (2021-2023). FNR is a widely used indicator for inferring near-surface O₃ sensitivity, with thresholds typically defined as: FNR < 1 for VOCs-limited, 1–2 for transitional, and >2 for NO_x-limited regimes (Jin et al., 2015; Hata et al., 2025; Rahman et al., 2025). The monthly FNRs reveal a consistent sub-seasonal evolution pattern across the three years. The spatial distributions transition from being dominated by blue grids (low FNR, VOCs-limited) in early summer to more green (transitional) and eventually yellow/red grids (NO_x-sensitive) by late summer, particularly evident in 2021 and 2022 (Fig. S6). At the basin scale, the mean FNR increases consistently from May to August, from 0.90 to 1.61 in 2021 and from 0.91 to 1.77 in 2022, reflecting a systematic seasonal shift toward more NO_x-limited O₃ formation (Table S3). Despite data gaps in May and August 2023, FNR values of 1.20 in June and 1.43 in July indicate a similar transition from transitional to more NO_x-sensitive conditions. Note that although column-based FNR is a useful indicator of surface O₃ sensitivity, satellite retrievals are subject to substantial uncertainties arising from measurement errors, cloud contamination, surface reflectivity, profile assumptions, and aerosol effects (Jin et al., 2017; Souri et al., 2023).

This independent, multi-year satellite evidence provides strong support for the central finding of our model-based analyses, namely a recurring sub-seasonal transition in O₃ formation regimes over the GZB, evolving from VOCs-limited conditions in early summer to transitional and ultimately NO_x-limited regimes by late summer. The consistency of this progression across years with contrasting meteorological conditions, including the extreme heat in 2022, indicates that the diagnosed regime shift is a robust characteristic of the regional photochemical environment. This behavior is therefore more plausibly driven by sub-seasonal factors, such as enhanced solar radiation, higher temperatures, and increased biogenic emissions, rather than by year-specific meteorological or emission anomalies.

3.3.2 Drivers of Temporal Shifts: Meteorology and Associated Chemistry

The temporal OFR transition from VOCs-limited to NO_x-limited is primarily

driven by evolving meteorology and chemistry from May to August. The AVOCs/NO_x emission ratios are relatively stable (0.27-0.34; Table S4) during the warm season. This variation cannot explain the stronger NO_x sensitivity detected in July–August, indicating that anthropogenic precursor ratios alone do not fully account for the seasonal OFR shifts. The most important change from May to August is the intensification of solar radiation and the resultant increase in air temperature. Firstly, BVOCs emissions are dependent on solar radiation and air temperature, so increased solar radiation and air temperature in mid-late summer boost BVOCs emissions, providing more background VOCs and pushing the O₃ formation toward NO_x-sensitive. Secondly, enhancement of solar radiation and higher temperature accelerate photochemical reactions. In addition, higher temperatures favor a deeper PBL, which enhances vertical mixing and can entrain O₃-rich air from aloft while diluting near-surface precursor concentrations and thus altering local precursor ratios. Near-surface O₃ concentrations tend to increase as the PBL height (PBLH) increases, peaking at the PBLH of approximately 900-1800 m (Wang et al., 2023). In urban areas of the GZB, the mean PBLH during 11:00-18:00 BJT rises from 1382 m in May to 1720 m in June, then falls to 1412 m in July and 1406 m in August, consistent with the maximum MDA8 O₃ level in June. Simulations indicate that HO_x radical concentrations increase while near-surface NO_x levels decrease from May to August in urban areas of the GZB (Fig. 5 and Table S5). These changes are closely linked to enhanced BVOCs emissions, intensified atmospheric photochemistry and PBL development, which alter relative balance of the O₃ precursor levels. Consequently, HO_x-loss becomes increasingly dominated by self-reaction of peroxy radicals rather than HO· + NO₂ termination, further shifting O₃ production to be more NO_x-sensitive.

The similar transition trend has been found in previous studies. Wu and Xie (2017) have discussed occurrence of a switch from a NO_x-saturated to NO_x-sensitive O₃ formation regime in most suburban and rural areas in China when summer arrives. Ou et al. (2016) have proposed that O₃ formation shifts toward VOCs-limited conditions in the PRD from summer to autumn. Sun et al. (2018) have used high-resolution observations in eastern China to show that the photochemical regime during spring

and summer tends toward NO_x -limited or mixed sensitivity, while in autumn and winter it shifts toward VOCs-limited conditions. Our study extends this understanding by resolving OFR transitions at sub-seasonal (monthly) and city-specific levels, offering feasible insights for dynamic emission control.

3.3.3 Drivers of Spatial Heterogeneity: Emissions and Transport

Spatial differences in OFR are closely tied to local emission profiles and regional transport. A key factor is the local VOCs (AVOCs + BVOCs) / NO_x emission ratio (Fig. 6). In early summer, XA, XY, WN, and TC had low ratios (2–7), leading to VOCs-limited regimes due to high NO_x emissions. In contrast, BJ's higher ratio (11–29) corresponds to NO_x -limited or transitional regimes. Notably, the strong VOCs sensitivity in WN is consistent with its relatively low VOCs/ NO_x ratio, reflecting elevated NO_x emissions from intensive power plant in the region. This pattern echoes observations in other heavily polluted Chinese cities, which often show strong VOCs sensitivity. These contrasts underscore that effective control strategies must account for both local emissions and inter-regional transport. This inflow elevates local NO_x (with relatively longer atmospheric lifetime than that of reactive VOCs) concentrations relative to VOCs, emphasizing the necessity of targeted AVOCs reductions before aggressive NO_x cuts can effectively mitigate O_3 pollution in this city.

These intra-region contrasts underscore that control strategies must be tailored to local chemistry. Similar patterns occur elsewhere: Ren et al. (2022) have found heavily polluted Chinese cities (e.g. Wuhan, Xi'an) are strongly VOCs-limited, whereas suburb and rural areas are NO_x -limited. Likewise, Yu et al. (2025) have diagnosed Zhengzhou's O_3 regime as primarily VOCs-limited, with an optimal ratio of VOCs to NO_x emission reductions of approximately 2.9:1, consistent with the strong VOC sensitivity observed in industrialized cities. Likewise, Yu et al. (2025) have diagnosed Zhengzhou's O_3 formation regime as primarily VOCs-limited, with an optimal VOCs-to- NO_x reduction ratio of approximately 2.9:1, consistent with the strong VOC sensitivity observed in industrialized cities.

Overall, these spatial and sub-seasonal OFR shifts highlight the necessity of dynamic, month-specific O_3 control strategies in the GZB. The pronounced VOCs-

limited conditions in early summer call for prioritizing AVOCs control, especially in cities with severe O₃ pollution like WN and XA, while the transition to NO_x-limited conditions by late summer favors NO_x-focused measures. Such temporally and spatially optimized approaches could enhance the efficiency of regional O₃ mitigation and help avoid unintended increases during seasonal transitions.

It is important to recognize that MDA8 O₃ variations in the EKMA diagrams integrate contributions from both local photochemical production and atmospheric transport and advection. Multiple recent modeling studies demonstrate that transport processes can contribute substantially to the regional ozone burden. For example, concentration and mass budget analyses show that horizontal advection from upwind regions and entrainment from the residual layer can supply a significant portion of ozone mass to a receptor region, especially during morning hours or under synoptic transport conditions, even if local photochemistry subsequently drives the daytime increase in surface ozone (Qu et al., 2023). However, the design of our EKMA simulations isolates the chemical sensitivity to precursor emissions by holding the meteorological fields and boundary conditions fixed across all scenarios. Because circulation and transport are invariant in this framework, changes in MDA8 O₃ arising from systematic reductions in NO_x and VOCs emissions reflect the in-situ chemical response of O₃ formation rather than changes in transport dynamics.

It is well-recognized that transport and advection represent a background forcing for region O₃ concentration. Studies of tropospheric O₃ precursors emphasize that long-range transport of O₃ and its precursors can influence surface O₃ trends and variability, and that such transport sets the baseline on which local chemistry operates. These transport influences can bias the placement of EKMA isolines in cases where background precursor concentrations (e.g., high transported NO_x or VOCs) differ substantially from typical values, potentially shifting the diagnosed sensitivity toward VOCs-limited or NO_x-limited regimes under certain conditions (Elshorbany et al., 2024). In this study, to mitigate the influence of transport and advection on EKMA results, we select representative O₃ polluted days that exclude anomalous episodes with unusually high backgrounds of transported O₃ and its precursor, such as strong

synoptic advection or intrusion events. Hence, the EKMA diagnostics predominantly capture the local chemical response to precursor perturbations under typical regional circulation patterns.”

