

Sub-seasonal and Spatial Variations in Ozone Formation and Co-control Potential for Secondary Aerosols in the Guanzhong Basin, Central China

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Abstract: Tropospheric ozone (O₃) pollution in warm seasons has become the key air-quality issue in the Guanzhong Basin (GZB), threatening human health despite prior successes in particulate matter control. Understanding how O₃ formation regimes (OFR) and secondary aerosol (SA) formation regimes (SAFR) evolve with time and space is critical for designing coordinated control strategies. Long-term near-surface observations (2014-2024) are combined with high-resolution WRF-Chem simulations for May-August 2022, employing scenario-based EKMA curves and source-apportionment diagnostics to resolve sectoral contributions. Results indicate a sub-seasonal OFR progression from VOCs-limited in early summer to transitional in midsummer and NO_x-limited in late summer, with anthropogenic contribution to the maximum daily averaged 8-h (MDA8) O₃ increasing from 32.8% in May to 55.2% in July and biogenic share peaking 18.7% in July. SAFR follows a distinct cycle with NO_x-limited in May, VOCs-limited in June, and transitional behavior thereafter. Traffic and industrial emissions are the dominant anthropogenic sources for both O₃ and SA. These patterns highlight phases of synergistic control, where anthropogenic VOCs mitigation in June and NO_x mitigation in August maximize co-benefits while minimizing trade-offs. This study integrated dynamic OFR/SAFR diagnostics with sectoral emission inventories can provide insights into pathways toward seasonally adaptive, city-specific air quality management in the GZB.

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1 Introduction

Tropospheric ozone (O_3), despite constituting only approximately 10% of total atmospheric O_3 , poses a significant threat to human health and ecosystem integrity (Valacchi et al., 2015; Feng et al., 2022). Long-term observations at regional background stations reveals a persistent upward trend in near-surface O_3 concentrations in China in recent decades (Wang et al., 2009; Sun et al., 2016; Xu et al., 2016). The nationwide implementation of the “Air Pollution Prevention and Control Action Plan” since September 2013 has achieved notable success in mitigating fine particulate matter ($PM_{2.5}$) pollution (Zheng et al., 2018; Zhang et al., 2019). However, O_3 pollution has emerged as a paramount challenge for air quality management in China during the warm season (May-August), driving extensive research on formation mechanisms and $PM_{2.5}$ co-control strategies (Li et al., 2019; Li et al., 2020; Liu et al., 2020; Wang et al., 2022; Wang et al., 2023; Wang et al., 2024).

Near-surface O_3 is a secondary pollutant formed through intricate photochemical reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOCs) under sunlight (Chapman, 1930; Chameides et al., 1992; Wang et al., 2017). The complex photochemical pathways of O_3 formation pose a significant barrier to effective O_3 pollution control, resulting in persistent high O_3 concentrations. The inherent nonlinearity in tropospheric O_3 formation necessitates the assessment of its Formation sensitivity Regime (OFR), which acts as a prerequisite for implementing effective control strategies. OFR is categorized into NO_x -limited, VOCs-limited, and transitional regimes according to the relationship of O_3 with its precursors (Lu et al., 2019). In NO_x -limited regimes, O_3 production is primarily terminated by self-reactions of peroxy radicals, reducing NO_x emissions effectively lowers O_3 . Conversely, in VOCs-limited regimes, termination occurs mainly via $NO_2 + HO\cdot$ reactions; reducing NO_x can slow $HO\cdot$ loss and reduce O_3 titration, resultantly increasing O_3 levels (Jenkin and Clemitshaw, 2000). Transitional regimes exhibit comparable sensitivity to both precursors. Current OFR assessment methods include indicator approaches (Sillman et al., 1995; Martin et al., 2004; Li et al., 2011), observation-based models (OBM) (Cardelino and Chameides, 1995; Wang et al., 2017; Song et al., 2022), and emission-based models (EBMs) utilizing three-dimensional chemical transport models (CTMs) (Li et al., 2018; Xu et al., 2022). Despite computational demands, EBMs provide a robust framework for resolving OFR across horizontal and vertical dimensions and over time, enabling direct investigation of OFR under varying meteorology and emission reduction scenarios (Ou et al., 2016; Wang et al., 2021).

Owing to the common precursors and complex interplay, synergistic control of $PM_{2.5}$ and O_3 has emerged as an essential priority for China’s air pollution mitigation in recent years (Xiao et al., 2021; Du et al., 2024; Kong et al., 2024). In addition to the common share of precursors (NO_x and VOCs), the ambient O_3 and its photochemical derivative, hydroxyl radicals ($\cdot OH$), constitute the major oxidants that oxidize precursors to form secondary aerosols (SA), such as sulfates, nitrates, and secondary organic aerosols (SOA). Moreover, hydroperoxyl radicals ($HO_2\cdot$), as a critical participate in O_3 production, whose concentration can be influenced by heterogeneous uptake on wet aerosol surfaces (Li et al., 2019; Wang et al., 2022). Furthermore, aerosol-radiation and aerosol-cloud interactions alter solar radiation and temperature in the atmosphere, thereby

influencing O₃ photochemical production (Baró et al., 2017; Li et al., 2019; Wu et al., 2020a). Therefore, optimizing precursor emission reductions requires not only understanding OFR but also the SA formation sensitivity regime (SAFR) to NO_x and VOCs. Integrating OFR and SAFR analyses under diverse meteorological conditions is critical to identifying co-beneficial pathways for simultaneously improving air quality.

The Guanzhong Basin (GZB), a key air pollution control area in central China, experiences severe warm-season O₃ pollution. Bei et al. (2022) have revealed that increased summertime unfavorable synoptic conditions are responsible for the deteriorated O₃ pollution in the GZB from 2014 to 2018. Biogenic emissions from extensive forests in Qinling mountains, situated south of the GZB, could interact with abundant anthropogenic emissions within the GZB when southerly winds prevail, facilitating O₃ formation in the region (Feng et al., 2016; Li et al., 2018; Dai et al., 2024). However, studies remain limited on the O₃ formation characteristics and the synergistic pollutants abatement in the region (Wang et al., 2022). This study employs a high-resolution online-coupled model to comprehensively resolve spatiotemporal patterns in warm-season O₃ formation characteristics and provide insights into O₃ pollution mitigation and synergistic air quality management in the GZB.

2 Methodology

2.1 The WRF-Chem model

The WRF-Chem model (Weather Research and Forecasting model with Chemistry) (Grell et al., 2005) utilized in this study is a specific version modified by Li et al (2010; 2011a; 2011b; 2012) and has been extensively used for regional simulations of air pollutants in the GZB. Simulations focus on the atmospheric processes over the GZB in the warm season of 2022. This period is selected for its exceptionally high O₃ pollution (with maximum daily averaged 8-h (MDA8) O₃ concentration of 134 µg m⁻³, +7% above the 2020-2024 mean), enabling a detailed analysis of photochemical mechanisms and co-control pathways. Figure 1 shows the model simulation domain encompassing the GZB and its surrounding regions, with particular focus on five major cities: Xi'an (XA, provincial capital), Xianyang (XY, undergoing rapid industrialization and urbanization), Weinan (WN, energy hub), Tongchuan (TC), and Baoji (BJ). Detailed model configuration can be found in S1 and Table S1 of the Supplementary Information (SI). This setup constitutes the base simulation, which serves as the reference for subsequent sensitivity scenarios.

2.2 Observations and Statistics for Comparisons

Observations of criteria pollutants (PM_{2.5}, NO₂, O₃, SO₂ and CO) released by China's Ministry of Ecology and Environment (MEE) are used for characterizing recent warm-season (2014-2024) air quality trends across the GZB and validating the simulated air pollutants. Meteorological parameters, including 2 m temperature, relative humidity, and 10-m wind speed/direction, measured at Jinghe station in the GZB (34.26°N and 108.58°E) are employed to evaluate the model performance in simulating synoptic conditions. Model performance of the base simulation is evaluated against observations

using statistical metrics including the mean bias (MB), root mean square error (RMSE), and the index of agreement (IOA, shown in S2 of the SI).

To evaluate the robustness of the simulated OFR, we have employed satellite-derived column densities of formaldehyde (HCHO) and NO₂. Daily Level-3 gridded HCHO data are obtained from the OMI/Aura HCHO Total Column Daily L3 Global 0.1°×0.1° product (OMHCHOD v003; NASA GES DISC). Daily Level-3 gridded NO₂ data are sourced from the OMI/Aura NO₂ Cloud-Screened Total and Tropospheric Column L3 Global 0.25°×0.25° product (OMNO2d v003; NASA GES DISC). A grid cell is excluded from the monthly average calculation if valid data are available for fewer than 8 days in that month.

2.3 Sensitivity simulations

Building upon the base simulation, an emission reduction matrix comprising 121 scenarios is then designed to develop EKMA diagrams to determine the O₃ and SA formation regime (Figure S1). These scenarios include reductions of NO_x and AVOCs emissions from 0% to 100% with an interval of 10%. Given that the biogenic VOCs (BVOCs) emissions are uncontrollable, only the AVOCs emission reduction is taken into consideration. It does not mean the insignificance of BVOCs in the O₃ formation. However, changes of plant cover and emissions as well as the O₃ uptake capacity of plants all affect the near-surface O₃ concentration through ecosystem-atmosphere interactions (Lin et al., 2020). The high-resolution, online-coupled WRF-Chem framework simulates all key processes affecting O₃ 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 O₃ concentrations. While the classical EKMA method based on O₃ 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). Furthermore, the brute force method (BFM) is used to evaluate the O₃ and SA contributions of industry, power, residential, transportation and biogenic sources in the GZB and five cities during the warm season of 2022. 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). 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.

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3 Results and Discussion

3.1 Air quality during warm seasons in the GZB

120 To understand the evolving characteristics of summertime photochemical pollution in the GZB, we first examine recent
trends in near-surface O₃ and PM_{2.5} concentrations during the warm seasons from 2022 to 2024. This period represents the
most recent stage of air quality management in the region and provides insight into ongoing challenges posed by secondary
pollutants. Under China's sequential air pollution policies—the Air Pollution Prevention and Control Action Plan (2013-2017;
State Council, 2013), the Three-Year Action Plan to Win the Blue-Sky War (2018-2020; State Council, 2018), and the Air
125 Quality Continuous Improvement Action Plan (2023-2025; MEE, 2023)—the GZB has achieved sustained PM_{2.5} reductions.
Warm-season PM_{2.5} concentrations have decreased from approximately 43.1 μg m⁻³ in 2014 to around 21.6 μg m⁻³ in 2024,
representing a nearly 50% reduction (Fig. 2a). In contrast, the mean MDA8 O₃ concentration during the warm season has
increased from 96.0 μg m⁻³ in 2014 to roughly 132.7 μg m⁻³ in 2024, with a substantial increase from 2014 to 2017, a decrease
from 2017 to 2020, followed by a renewed upward trend thereafter (Fig. 2b). While the substantial alleviation in the particulate
130 pollution is mainly due to the anthropogenic emission mitigation, O₃ pollution has worsened in the region primarily driven by
increased unfavorable conditions and secondarily by changes in anthropogenic emissions (Bei et al., 2022). Near-surface
observations have revealed persistent O₃ pollution during the warm season, with frequent exceedances of the national ambient
air quality standard for MDA8 O₃ (160 μg m⁻³, as shown in Table 1). Year-to-year fluctuations in mean MDA8 O₃ levels are
governed by the frequency of exceedances, which rise from 8.3% in 2014 to 36.7% in 2017, fall to 13.6% in 2020, and climb
135 again to 27.0% in 2024; the magnitude of those exceedances remains relatively stable, ranging from 178 to 189 μg m⁻³ (Table
1).

The monthly evolution of O₃ concentrations reveals a pronounced sub-seasonal pattern in the GZB. June consistently
emerges as the peak month for both MDA8 O₃ levels and exceedance frequency (Fig. S5 and Table S2). During the warm
seasons from 2014 to 2024, the mean MDA8 O₃ concentration in June reaches approximately 132 μg m⁻³, with over 30% of
140 days with O₃ exceedances. The peak corresponds closely with meteorological conditions typically observed in early summer,
when the region experiences strong solar radiation, elevated temperatures, and relatively low precipitation conditions that are
highly conducive to photochemical O₃ formation (Pay et al., 2019). The early-summer O₃ peak observed in the GZB is
consistent with reports from northern China, where June maxima are evident in the Beijing–Tianjin–Hebei (BTH) region and
June–July peaks prevail across the North China Plain (Han et al., 2020; Li et al., 2020). In contrast, in southern China, O₃ sub-
145 seasonality is strongly modulated by subtropical high-pressure systems, the East Asian monsoon, typhoon passages, and land–
sea breeze circulations. As a result, the peak O₃ episodes are tended to emerge in May or during the late summer to early
autumn (September–October) in the Yangtze River Delta (YRD) and Pearl River Delta (PRD) (Han et al., 2020; Xu et al.,
2020; Ouyang et al., 2022). These regional contrasts highlight that while the precise timing of seasonal O₃ peaks is shaped by
local climate and meteorology, the emergence of a distinct sub-seasonal maximum is a robust feature across China's major
150 urban clusters. This underscores the sensitivity of regional air quality to meteorological transitions and highlights the need for
sub-seasonally adaptive control strategies, in particularly during the high-risk period.

How these basin-wide trends manifest at the city scale is then explored. O₃ variations in all five cities mirror the overall pattern in GZB, with MDA8 O₃ concentrations rising from 2014 to a maximum in 2017 and then dipping through 2020 before climbing again to 2024 levels. Cities of XA, XY, and WN, located in the central GZB, have the relatively high O₃ levels, with the mean MDA8 O₃ concentration ranging of 128-129 µg m⁻³ during the warm seasons of 2014-2024. XY has experienced the fastest MDA8 O₃ concentration increase of 6.3 µg m⁻³ yr⁻¹, nearly twice the basin average of 3.7 µg m⁻³ yr⁻¹, which likely reflects rapid urban expansion and increasing local precursor emissions. The city also records the highest fraction of exceedance days, averaging 28.7% of warm-season days during 2014–2024 and peaking at 49.2% in 2017 (Table 1). XA is also characterized by the sever O₃ pollution comparing with other cities, with a growth rate of 3.8 µg m⁻³ yr⁻¹ and exceedances on 25.9% of the warm-season days, consistent with its role as the region’s primary emission hub. By contrast, BJ, situated on the western edge and often upwind of the basin core, had the lowest O₃ burden, with the mean MDA8 O₃ concentration of 113.3 µg m⁻³ and only 10.9% exceedances of warm-season days during 2014-2024. These spatial differences underscore the importance of both local precursor controls in rapidly urbanizing cities and regional transport pathways in shaping O₃ pollution across the GZB.

Generally, the long-term observations reveal not only a basin-wide deterioration in O₃ pollution but also strong sub-seasonal and spatial heterogeneity, highlighting the necessity of process-based modeling to resolve spatiotemporal patterns in warm-season O₃ formation characteristics and to provide insights into air pollution mitigation in the GZB.

3.2 Model validation

The meteorological simulations during the warm season of 2022 demonstrate excellent reproduction of diurnal temperature patterns (IOA = 0.99) despite slight overestimation biases (+0.4 °C), while relative humidity variations are well captured (IOA = 0.95) with marginal underestimation (-1.8%, Fig. S2). Spatially, the model reproduces key air pollutants distributions across the GZB against measurements (Fig. S3). Elevated PM_{2.5} and O₃ in the eastern and central regions arise from northeasterly transport, weak winds over the central basin plain that favor accumulation of air pollutants, and southerly flows carrying BVOCs from the Qinling forests. Temporally, simulated air pollutant concentrations show good agreement with observations with IOAs all exceeding 0.5 (Fig. S4). The model’s good performance in replicating synoptic-scale meteorological processes and associated air pollutants warrants its suitability for mechanistic analysis. Comprehensive validation of the WRF-Chem model performance is detailed in S3 of the SI.

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 precursors. 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-

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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 HO₂ + 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.

删除了： EKMA curves reveal pronounced spatiotemporal shifts in OFR. In May and June, the GZB as a whole was predominantly VOCs-limited, indicating that AVOCs reductions would substantially lower O₃ concentrations, whereas moderate NO_x cuts could exacerbate O₃ pollution (Figs. 3a and 3b). City by city, however, sensitivity varied. O₃ formation in BJ lies in a VOCs-sensitive regime close to the transitional zone, where initial reductions in either NO_x or AVOCs emissions lead to decreases in MDA8 O₃ concentrations (Fig. 4a5). O₃ concentrations exhibit greater sensitivity to reductions in AVOCs emissions before precursor emissions being cut by approximately 50%. WN occupies the most NO_x-saturated zone of the GZB in May and June under current emissions: with 100% AVOCs emissions, a 60% cut in NO_x emissions results in 11.7% and 9.3% increases in urban MDA8 O₃ concentrations in May and June, respectively (Figs. 4a3 and 4b3).

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删除了： By July, OFR in urban areas of the GZB shifts toward the transitional regime (Fig. 3c). Under current AVOCs emissions, a NO_x reduction exceeding 10% is sufficient to achieve a notable decrease in MDA8 O₃ concentration. All five cities show movement toward less VOCs-sensitive regimes (Fig. 4c). O₃ formation in XA and WN remains primarily AVOCs-controlled, whereas it in XY, TC, and BJ becomes transitional. Ordering the cities with OFR varying from most VOCs-sensitive to most NO_x-sensitive conditions yields the sequence that WN > XA > TC > XY > BJ. In August, OFR in the GZB enters a NO_x-limited regime (Fig. 3d): a 40% NO_x emission mitigation delivers an average MDA8 O₃ decrease of 11.1%, whereas an equal AVOCs reduction yields only a 3% decrease. OFRs in all cities except in WN (transitional) are NO_x-limited (Fig. 4d), indicating that initial NO_x reductions represent the most effective mitigation pathway to alleviate O₃ pollution.

The temporal OFR shifts can be attributed to concurrent changes in chemistry and meteorology. The AVOCs/NO_x emission ratios are relatively stable (0.27-0.34; Table S3) 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 shift. The most important change from May to August is the intensification of solar radiation and the resultant increase in air temperature. Firstly, BVOCs ... [1]

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360 reflecting elevated NO_x emissions from intensive power plant in the region. This pattern echoes observations in other heavily
365 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 O₃ pollution in this city.

365 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 O₃ 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 O₃
370 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 O₃ 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 efficacy of regional O₃ mitigation and help
375 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
380 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
385 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
390 substantially from typical values, potentially shifting the diagnosed sensitivity toward VOCs-limited or NO_x-limited regimes

删除了： Spatially, OFRs varied markedly among cities in relation to local VOCs (AVOCs + BVOCs) / NO_x emission ratios (Fig. 6). In early summer, XA, XY, WN and TC all have relatively lower ratios (within 2 to 7) and exhibit VOCs-limited regimes, indicating their high NO_x emissions make O₃ formation strongly VOCs-constrained. By contrast, BJ generally falls within the NO_x-limited or transitional regimes (except in June) with relatively high VOCs/NO_x ratio ranging from 11 to 29, suggesting comparatively lower NO_x concentration or/and relatively higher VOCs levels. OFR in WN exhibits the most NO_x-saturated (VOCs-limited) characteristics, even though its VOCs/NO_x emission ratio is not the lowest—in part because WN lies on the eastern margin of the GZB and is susceptible to pollutant transport from heavily polluted regions in Henan and Shanxi (Li et al., 2021). 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 O₃ pollution in this city. These intra-region contrasts underscore that control strategies must be tailored to local chemistry. Spatially, OFRs varied markedly among cities in relation to local VOCs/NO_x emission ratios (Fig. 6). In early summer, XA, XY, WN, and TC all had low VOCs/NO_x ratios (~2–7) and exhibited VOCs-limited regimes, indicating their high NO_x emissions made ozone formation strongly VOCs-constrained. By contrast, BJ's much higher VOCs/NO_x ratio (11–29) placed it in NO_x-limited or transitional regimes. Notably, WN was the most NO_x-saturated city, even though its VOCs/NO_x was not the absolute lowest – in part because WN lies on the GZB's eastern margin and is affected by pollutant transport from heavily polluted northern regions. The inflow of NO_x-rich air elevates local NO_x relative to VOCs, reinforcing VOCs-limited chemistry in WN. These intra-region contrasts underscore that control strategies must be tailored to local chemistry. Similar patterns occur elsewhere: Ren et al. (2022) found heavily polluted Chinese cities (e.g. Wuhan, Xi'an) were strongly VOCs-limited, whereas suburb and rural areas were NO_x-limited. Likewise, Yu et al. (2025) diagnosed Zhengzhou's ozone regime as primarily VOCs-limited with an optimal VOCs : NO_x reduction ratio of ~2.9:1, echoing the high VOCs-sensitivity we see in industrial cities.

435 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.

3.4 Sectoral Contributions to Warm-Season O₃ Production

440 Quantifying sectoral drivers of warm-season O₃ production bridges the sensitivity diagnostics from Section 3.2 with
operational emission control design. The MDA8 O₃ contributions of industrial, residential, traffic, power plants and biogenic
sources are assessed from May to August using the BFM (Figs. 7 and 8).

445 The attribution results show pronounced spatiotemporal heterogeneous across the GZB. At the basin scale, the
contribution of all anthropogenic sources increases from 32.8% in May to 55.2% in July, then declines to 48.0% in August
(Fig. 7). The rise is largely driven by increasing industrial and traffic influence: industrial emissions contribute 5.4% to MDA8
O₃ in May, rising to 11.8% in July, while traffic contributions increase from 5.8% to 17.0% during the same period (Fig. 8 and
Table 3). Because NO_x and AVOCs emissions peak in June and then decline, the continued anthropogenic contribution growth
through July indicates that enhanced photochemical activity under strong solar radiation and rising BVOCs emissions further
amplify O₃ formation. Biogenic contributions notably rise from 9.7% in May to 18.7% in July then slightly decline to 16.7%
in August (Fig. 7 and Table 3), consistent with elevated BVOCs emissions under warmer, sunnier conditions. These sub-
450 seasonal dynamics are consistent with findings from other Chinese urban clusters, such as the BTH, YRD and PRD, where
rising BVOCs emissions in summer have been shown to enhance photochemical reactivity and partially offset gains from
anthropogenic VOCs and NO_x reductions, thereby promoting shifts of OFR toward NO_x-limited or transitional regimes (Wu
et al., 2020b; Zhao et al., 2022; Gao et al., 2025; Wang et al., 2025).

455 Spatial contrasts across the five cities further illustrate how emission profiles interact with chemical regimes and guide
targeted mitigation policies. XA and XY show the largest anthropogenic O₃ shares, rising from 37.1% in May to 58.7% in July
in XA, and from 35.7% to 59.2% in XY (Fig. 7 and Table 3). In these urban cores, industrial and traffic emissions are dominant,
contributing approximately 9-12% (May) and 26-31% (June-August) to MDA8 O₃ concentrations (Fig. 8). TC and BJ show
intermediate anthropogenic contributions. Traffic dominates their O₃ production (7.1-15.9% in TC and 7.9-18.3% in BJ), and
industrial emissions are the secondary contributor to the O₃ levels. Given their VOCs-limited regime (Section 3.2) and higher
460 industrial AVOCs emissions (Table S5) in May–June, prioritizing reductions in industrial AVOCs is advisable to prevent O₃
rebound. As the OFR shifts toward transition and NO_x-limited conditions in late summer, mitigation efforts should be
combined with traffic emissions due to the higher NO_x share from vehicular exhaust. In industrial regions, for instance, Dai
et al. (2025) have showed that oxygenated VOCs (OVOCs) contribute a high proportion (~30–37.8%) of VOCs pools in
industrial cities, enhancing radical production and O₃ sensitivity; thus, control strategies must consider VOCs speciation, not

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just total amounts. By contrast, WN exhibits much lower anthropogenic influence (13.9–34.7%, Fig. 7 and Table 3), with power plant emissions exerting a net consuming effect on local O₃. This is attributed to strong local NO titration and enhanced termination pathways reduce OH/HO₂ recycling. Similar suppression effects have been reported in Zhao et al. (2025) that power plant NO_x emissions contribute negative O₃ signals in certain regions, indicative of O₃ titration under saturating NO_x.
470 Meanwhile, analyses in the YRD have showed that during emission reductions, weakened NO titration can drive O₃ increases (~20% of the rise attributed to reduced NO titration) (Wang et al., 2022). Mechanistic modeling also indicates that NO_x reductions in VOCs-limited areas may lead to O₃ increases, unless VOCs controls are pursued simultaneously (Dai et al., 2024; Tang et al., 2021). Therefore, aggressive NO_x cuts alone risk raising O₃ unless paired with targeted AVOCs reductions in WN.

These variations highlight that a uniform, time-invariant control strategy is insufficient. Instead, effective O₃ mitigation
475 in the GZB demands sub-seasonally adaptive, sector-specific emission controls. In early summer, dominant VOCs sensitivity suggests focusing on industrial AVOCs; in mid to late summer, integrating AVOCs and traffic NO_x controls aligns better with evolving regimes; and in regions like WN, VOCs-targeted strategies must accompany any NO_x reductions. Recent studies similarly argue that tailoring precursor reductions to local O₃ regimes yields greater benefits than uniform cuts. For example, Zhu et al. (2022) showed that in the NCP and YRD, formation regimes have shifted from VOCs-limited toward transitional or
480 NO_x-limited states as atmospheric oxidation increases. Wang et al. (2025) reported pronounced vertical and spatial differences in OFRs in eastern Chinese cities, implying that a one-size-fits-all control is often suboptimal. Li et al. (2024) have used FNR (HCHO/NO₂) diagnostics at multiple altitudes to reveal that optimal precursor strategies vary by vertical layer in the BTH.

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.

3.5 Synergistic Control of O₃ and Secondary Aerosols

3.5.1 Impacts of Aerosol-Radiation-Chemistry Interactions

The substantial decline in PM_{2.5} mass in the GZB over the past decade raises the question of whether aerosol-radiation and aerosol-chemistry interactions have notably influenced the observed increase in warm-season O₃ and possibly modulated its formation sensitivity. To quantify these effects, we conduct sensitivity experiments to separately isolate (i) aerosol-induced radiative changes (A_Rad) and (ii) changes in heterogeneous HO₂ uptake on wet aerosol surfaces (A_HO₂) associated with aerosol loading variations during the warm season from 2014 to 2022. In the A_Rad experiment, all model configurations are identical to the base simulation, except that aerosol concentrations within the PBL are fixed at their 2014 levels in the aerosol-radiation transfer module. Similarly, in the A_HO₂ experiment, aerosol concentrations are fixed at 2014 levels only in the calculation of heterogeneous HO₂ uptake on wet aerosol surfaces, while all other processes remained unchanged. The resulting differences from the base case therefore represent the impacts of aerosol changes between 2014 and 2022 on MDA8 O₃ through radiative and HO₂ heterogeneous loss pathways, respectively.

Over the period 2014–2022, during which observed PM_{2.5} concentrations in the GZB have declined by approximately 21.4 μg m⁻³, the A_Rad and A_HO₂ effects exerted comparable influences on MDA8 O₃, each contributing between 3 and 7 μg m⁻³ across most of the region. The combined influence of these two pathways results in an increase of approximately 4.0 μg m⁻³ in the mean warm-season MDA8 O₃ concentration over the GZB, with peak enhancements exceeding 7 μg m⁻³ in urban core areas with high aerosol levels during June and July (Fig. 9). Although non-negligible, this aerosol-mediated increase accounts for only 10.4% of the total observed MDA8 O₃ rise (38.14 μg m⁻³) during the warm seasons from 2014–2022 over the GZB. Thus, while the PM_{2.5} cleanup has exerted a discernible upward pressure on O₃ via enhanced photochemistry and modified radical cycling, it is not the dominant driver of the worsening O₃ pollution; the primary factors remain the increased frequency of unfavorable synoptic conditions and changes in anthropogenic precursor emissions (Bei et al., 2022; Zhao et al., 2026).

A key follow-up question is whether these aerosol effects alter the identification of sub-seasonal OFRs. Additional sensitivity simulations for 2022, in which A_Rad and A_HO₂ are deliberately switched off, show that the combined A_Rad+A_HO₂ effect modestly suppresses MDA8 O₃ concentrations by 0.1–1.0 μg m⁻³ under current emission levels but does not change the fundamental spatiotemporal progression of the O₃ formation sensitivity (Fig. S7). This indicates that the chemical sensitivity of O₃ production to its precursors is primarily governed by the evolving balance between NO_x and VOCs under the prevailing meteorology, rather than by aerosol-mediated perturbations under contemporary pollution levels.

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Therefore, although the historical PM_{2.5} reduction has provided a modest boost to O₃ concentrations, it has not reshaped the intrinsic, meteorologically-driven transitions in OFR. This finding supports the use of OFR diagnostics, which are largely insensitive to aerosol loading in the current environment, as a reliable basis for designing seasonally adaptive control strategies.

3.5.2 Spatiotemporal Patterns of Secondary Aerosol Formation Sensitivity

While summertime air quality in the GZB is dominated by O₃ pollution, SA remain non-negligible even when PM_{2.5} is relatively low. Warm-season SAFR diagnostics show clear seasonal shifts (Figs. 3 and 10). At the basin scale, SA is NO_x-limited in May, with reductions in NO_x emissions delivering roughly three times the concentration decreases in SA compared to equivalent mitigation in AVOCs emissions (Fig. 3e). In June, the regime shifts to VOCs-limited, with benefits from AVOCs emission reductions outweighing those from NO_x controls (Fig. 3f). In July, SAFR exhibits a transitional state with sensitivity varying by location, whereas in August it reverts to a transitional regime tilted toward NO_x sensitivity (Figs. 3g and 3h). City-level patterns follow this broad seasonal evolution but reveal important local deviations (Fig. 10): in June, XA, XY, WN, and TC are VOCs-limited, whereas BJ remains transitional. SAFR of WN stands out by retaining VOCs sensitivity into July, albeit weaker than in June, while other cities transition earlier. By August, SAFR of all cities exhibit transitional responses with a leaning toward NO_x sensitivity, indicating that late summer presents an opportunity for NO_x-focused co-control.

The observed spatiotemporal evolution of SAFR can be interpreted in the context of the seasonal progression of key chemical and meteorological drivers. The NO_x-limited regime in early summer is likely associated with an enhanced contribution of nitrate to secondary aerosols, under conditions where SA formation remains sensitive to NO_x through HNO₃ production and subsequent gas–particle partitioning favored by relatively lower temperatures, higher humidity, and weaker photochemical activity. As solar radiation and temperature increase in June, the enhanced atmospheric oxidation capacity, together with temperature-dependent VOCs and biogenic emissions, promotes SOA formation, leading to a shift toward a VOCs-limited SAFR. The persistent VOCs sensitivity in WN into July reflects its relatively high NO_x emissions, which decrease the local VOCs/NO_x ratio and thereby reinforce VOCs-limited chemistry. By late summer (August), warmer and more humid conditions increase aerosol liquid water content and favor efficient nitrate formation and partitioning, contributing to a renewed tendency toward NO_x-sensitive SAFR.

Source attributions show anthropogenic sources dominate SA formation (63-87%) across the GZB, with traffic and industry are principal contributions (Table 3). Power plant emissions are particularly influential in WN, where their NO_x emissions drive elevated SA formation, while simultaneously exerting a local O₃-suppressing effect. Residential emissions contribute moderately, ranging from 7–22% across cities and months, while biogenic sources play a relatively minor role in SA formation.

3.5.3 Implications for Seasonally Adaptive Control Strategies

Considering the multifaceted interactions between O₃ and SA, changes in one pollutant often propagate to the other, making it essential to consider them within a unified management framework. During the warm season, when photochemical

删除了： While summertime air quality in the GZB is dominated by O₃ pollution, SA remain non-negligible even when PM_{2.5} is relatively low. The interaction between O₃ and SA is multifaceted: O₃ and SA are closely linked through shared precursors and atmospheric oxidation processes. Elevated O₃ levels enhance the formation of SA by increasing the oxidizing capacity of the atmosphere, thereby accelerating the conversion of gaseous precursors into both inorganic and organic aerosol components. Yu et al. (2025) have noted that secondary organic carbon increases when O₃ exceeding 50 μg m⁻³, indicating stronger photochemistry yields more SOA. Conversely, by scattering or absorbing radiation, aerosols can change the intensity and spectral distribution of light, thereby modulating photolysis rates (Wu et al., 2019; Wu et al., 2020). In addition, aerosol surfaces can facilitate or suppress specific chemical reactions—such as the conversion of NO₂ to nitrate or the uptake of hydroperoxyl radicals—which in turn influence O₃ production and loss pathways (Li et al., 2019; Wang et al., 2022). These bidirectional interactions mean that changes in one pollutant often propagate to the other, making it essential to consider them within a unified management framework. During the warm season, when photochemical activity peaks and O₃ dominates air pollution, incorporating SA considerations into O₃-focused control strategies can provide additional air quality benefits and help prevent counterproductive effects on pollutant levels.

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590 activity peaks and O₃ dominates air pollution, incorporating SA considerations into O₃-focused control strategies can provide
additional air quality benefits and help prevent counterproductive effects on pollutant levels. In May, SAFR is strongly NO_x-
limited while O₃ is VOCs-limited, indicating that NO_x reductions would decrease SA, but VOCs-focused measures must be
maintained to avoid O₃ rebounds. In June, both pollutants are VOCs-sensitive in most cities, making AVOCs reductions
(industry + traffic) especially beneficial. In July, XA, XY, TC, and BJ occupy broader transitional zones, where reductions in
NO_x and AVOCs emissions both can yield benefits; WN's lingering VOC sensitivity suggests AVOC-focused strategies
595 remain prioritized there. By August, SAFR in all cities tilting toward NO_x sensitivity and O₃ is largely NO_x-limited, suggesting
that NO_x reductions—particularly from power plants and traffic exhausts—become the most effective co-control approach.

From a policy perspective, warm-season air quality management in the GZB should adopt sub-seasonal sequencing
emission controls. AVOCs reductions from traffic and industrial sources are prioritized in early summer, combined NO_x-
AVOCs strategies in transitional regimes are required in mid-summer, and NO_x reductions to maximize co-benefits for both
600 O₃ and SA are emphasized in late summer. Embedding SA considerations into an O₃-focused framework allows decision-
makers to capitalize on synergistic effects where they naturally arise, while avoiding unintended pollutant trade-offs, ultimately
providing a more efficient pathway toward cleaner warm season air in the GZB.

4 Summary

This study combines long-term near-surface observations and high-resolution WRF-Chem simulations to diagnose
605 summertime O₃ formation and its source attributions across the GZB, and to explore co-control potential with SA.
Observational analyses show a nearly 50% decline in PM_{2.5} mass concurrent with a marked rise in MDA8 O₃ concentrations
and increasing O₃ exceedance frequency during warm seasons from 2014 to 2024, with June as the climatological O₃ peak
month.

Incorporating an EKMA framework and BFM into WRF-Chem to simulate warm-season O₃ pollution in 2022, we find
610 pronounced spatiotemporal shifts in OFR across the GZB: predominantly VOCs-limited in May–June, shifting toward
transitional in July, and becoming NO_x-limited in August. Sectoral attribution indicates contribution of anthropogenic sources
to MDA8 O₃ concentrations rises from 32.7% to 55.2% (July), with biogenic shares peaking (18.7%) in July. City-level
differences are notable—XA and XY are high anthropogenic cores with large industrial and traffic influences, WN shows the
most and persistent VOCs-limited / NO_x-saturated behavior, while BJ on the western edge is comparatively less polluted and
615 more NO_x-limited or transitional. SAFR diagnostics shows a different seasonal pattern: the SAFR is NO_x-limited in May,
VOCs-limited in June, transitional in July, and transitional with a NO_x-leaning sensitivity in August across the GZB. Traffic
and industry emerge as primary contributors to both O₃ and SA, while power plants strongly influence SA in WN.

删除了： These findings point to several opportunities for achieving synergistic O₃-SA control.

620 Based on these findings, we recommend sub-seasonally adaptive, city-specific control strategies: prioritize reductions of
AVOCs, particularly from industrial and traffic sources, during early summer (notably June) to capture a VOCs-led co-benefit
opportunity; implement combined NO_x-AVOCs emission mitigation measures during the transitional month (July); and
emphasize NO_x mitigation from traffic, power plants emissions in late summer (August) to maximize co-benefits for both O₃
and SA while minimizing unintended trade-offs. Integrating real-time OFR and SAFR diagnostics with source attributions will
625 enhance the efficiency and resilience of warm-season air quality management in the GZB.

Acknowledgments. This work is financially supported by the National Natural Science Foundation of China grant 42307154,
the Key Research and Development Program of Shaanxi grant 2024SF-ZDCYL-05-05 and the China Postdoctoral Science
Foundation grant 2023M743462.

630 **Code and data availability.** The hourly ambient surface O₃, NO₂ and PM_{2.5} mass concentrations are real-timely released by
Ministry of Environmental Protection, China on the website <http://www.aqistudy.cn/> (China MEP, 2013; last access: 20 August
2025). Observations of the near surface meteorological factors are released from <http://www.meteomanz.com> (last access: 23
August 2025).

Author contributions. NZ, as the corresponding author, provided the ideas, verified the conclusions, and revised the paper.
635 RW conducted research, designed the experiments, performed the simulation, processed the data, prepared the data
visualization, and prepared the manuscript, with contributions from all authors. JW provided the primary data processing and
reviewed the manuscript. JY, QJ, and YL analyzed the initial simulation data and visualized the model results. XT reviewed
the manuscript and provided critical reviews.

Competing interests. The authors declare that they have no conflict of interest.

640 **References**

- Baró, R., Palacios-Peña, L., Baklanov, A., Balzarini, A., Brunner, D., Forkel, R., Hirtl, M., Honzak, L., Jiménez-Guerrero, P., Langer, M., Pérez, J. L., Pirovano, G., San José, R., Rodríguez, S., and Tuccella, P.: Regional effects of atmospheric aerosols on temperature: an evaluation of an ensemble of online coupled models, *Atmos. Chem. Phys.*, 17, 9677–9696, doi:10.5194/acp-17-9677-2017, 2017.
- 645 Bei, N., Liang, J., Li, X., and Wang, R.: Worsening summertime ozone pollution in the Guanzhong Basin, China from 2014 to 2018: impacts of synoptic conditions and anthropogenic emissions, *Atmos. Environ.*, 274, 118974, doi:10.1016/j.atmosenv.2022.118974, 2022.
- Cardelino, C. A. and Chameides, W. L.: An observation-based model for analyzing ozone precursor relationships in the urban atmosphere, *J. Air Waste Manage. Assoc.*, 45, 161–180, doi:10.1080/10473289.1995.10467354, 1995.
- 650 Chameides, W. L., Fehsenfeld, F., Rodgers, M. O., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D. R., Rasmussen, R. A., and Zimmerman, P.: Ozone precursor relationships in the ambient atmosphere, *J. Geophys. Res.*, 97, 6037–6055, doi:10.1029/91JD03014, 1992.
- Dai, J., Brasseur, G. P., Vrekoussis, M., Kanakidou, M., Qu, K., Zhang, Y., Zhang, H., and Wang, T.: The atmospheric oxidizing capacity in China – Part 2: Sensitivity to emissions of primary pollutants, *Atmos. Chem. Phys.*, 24, 12943–12962, <https://doi.org/10.5194/acp-24-12943-2024>, 2024.
- 655 Dai, J., Zhang, K., Feng, Y., Yi, X., Li, R., Xue, J., Li, Q., Shi, L., Liao, J., Yi, Y., Wang, F., Yang, J., Chen, H., Huang, L., Tan, J., and Wang, Y.: Significant influence of oxygenated volatile organic compounds on atmospheric chemistry: a case study in a typical industrial city in China, *Atmos. Chem. Phys.*, 25, 7467–7484, <https://doi.org/10.5194/acp-25-7467-2025>, 2025.
- Dai, W., Wang, R., Zhong, H., Li, L., Zhang, Y., Li, J., Huang, T., and Tie, X.: Impact of formaldehyde on ozone formation in Central China: important role of biogenic emission in forest region, *Sci. Total Environ.*, 949, 175182, doi:10.1016/j.scitotenv.2024.175182, 2024.
- 660 Du, S., He, C., Zhang, L., Zhao, Y., Chu, L., and Ni, J.: Policy implications for synergistic management of PM_{2.5} and O₃ pollution from a pattern–process–sustainability perspective in China, *Sci. Total Environ.*, 916, 170210, doi:10.1016/j.scitotenv.2024.170210, 2024.
- 665 Dunker, A. M., Morris, R. E., Pollack, A. K., Schleyer, C. H., and Yarwood, G.: Photochemical modeling of the impact of fuels and vehicles on urban ozone using Auto/Oil Program data, *Environ. Sci. Technol.*, 30, 787–801, doi:10.1021/es9502340, 1996.
- 670 [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.](#)
- Feng, T., Bei, N., Huang, R., Liu, S., Wang, Q., Xue, M., and Li, G.: Summertime ozone formation in Xi’an and surrounding areas, China, *Atmos. Chem. Phys.*, 16, 4323–4342, doi:10.5194/acp-16-4323-2016, 2016.
- 675 Gao, C., Zhang, X., Lun, X., Gao, Y., Guenther, A., Zhao, H., Zhang, S., Huang, L., Song, K., Huang, X., Gao, M., Ma, P., Jia, Z., Xiu, A., and Zhang, Y.: BVOCs' role in dynamic shifts of summer ozone formation regimes across China and policy implications, *J. Environ. Manage.*, 376, 124150, <https://doi.org/10.1016/j.jenvman.2025.124150>, 2025.
- Han, H., Liu, J., Guo, S., Tan, Q., Li, J., Li, Y., and Mao, H.: Formation mechanisms of a severe ozone episode over Beijing–Tianjin–Hebei and its implications for ozone control strategies in summer, *Atmos. Chem. Phys.*, 20, 4399–4414, <https://doi.org/10.5194/acp-20-4399-2020>, 2020.

- 680 [Hata, H., Inoue, K., Yoshikado, H., Genchi, Y., and Tsunemi, K.: Impact of introducing electric vehicles on ground-level O₃ and PM_{2.5} in the Greater Tokyo Area: yearly trends and the importance of changes in the Urban Heat Island effect, *Atmos. Chem. Phys.*, **25**, 1037–1056, <https://doi.org/10.5194/acp-25-1037-2025>, 2025.](#)
- Jenkin, M. E. and Clemitshaw, K. C.: Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer, *Atmos. Environ.*, **34**, 2499–2527, doi:10.1016/S1352-2310(99)00478-1, 2000.
- 685 [Jin, X., and Holloway, T.: Spatial and temporal variability of ozone sensitivity over China observed from the Ozone Monitoring Instrument, *J. Geophys. Res.-Atmos.*, **120**, 7229–7246, <https://doi.org/10.1002/2015JD023250>, 2015.](#)
- [Jin, X., Pusede, E. A., Wiedinmyer, C. J., Fischer, M. L., and Oetjen, H. J.: Evaluating a space-based indicator of surface ozone–NO_x–VOC sensitivity over midlatitude source regions and application to decadal trends, *J. Geophys. Res.-Atmos.*, **122**, 10451–10471, <https://doi.org/10.1002/2017JD026720>, 2017.](#)
- 690 Kong, L., Song, M., Li, X., Liu, Y., Lu, S., Zeng, L., and Zhang, Y.: Analysis of China’s PM_{2.5} and ozone coordinated control strategy based on the observation data from 2015 to 2020, *J. Environ. Sci.*, **138**, 385–394, doi:10.1016/j.jes.2023.05.015, 2024.
- Li, K., Jacob, D. J., Liao, H., Zhu, J., Shah, V., Shen, L., Bates, K. H., Zhang, Q., and Zhai, S.: Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, *Proc. Natl. Acad. Sci. USA*, **116**, 422–427, doi:10.1073/pnas.1812168116, 2019.
- 695 Li, K., Jacob, D. J., Shen, L., Lu, X., De Smedt, I., and Liao, H.: Increases in surface ozone pollution in China from 2013 to 2019: anthropogenic and meteorological influences, *Atmos. Chem. Phys.*, **20**, 11423–11433, doi:10.5194/acp-20-11423-2020, 2020.
- Li, L., Chen, C., Huang, C., Huang, H., Zhang, G., Wang, Y., and Wang, H.: Ozone sensitivity analysis with the MM5-CMAQ modeling system for Shanghai, *J. Environ. Sci.*, **23**, 1150–1157, doi:10.1016/S1001-0742(10)60531-0, 2011.
- 700 Li, N., He, Q., Greenberg, J., Guenther, A., Li, J., Cao, J., Wang, J., Liao, H., Wang, Q., and Zhang, Q.: Impacts of biogenic and anthropogenic emissions on summertime ozone formation in the Guanzhong Basin, China, *Atmos. Chem. Phys.*, **18**, 7489–7507, doi:10.5194/acp-18-7489-2018, 2018.
- [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.
- 705 Li, Q., Zhang, L., Wang, T., Wang, Z., Fu, X., and Zhang, Q.: “New” reactive nitrogen chemistry reshapes the relationship of ozone to its precursors, *Environ. Sci. Technol.*, **52**, 2810–2818, doi:10.1021/acs.est.7b05794, 2018.
- [Li, Y., Gao, M., Liu, Y., Wang, Y., Zhang, L., Chen, X., and Wang, T.: Ozone formation sensitivity at various altitudes: seeking the best control strategies in the Beijing–Tianjin–Hebei region, *Environ. Sci. Technol. Lett.*, **11**, 785–791, <https://doi.org/10.1021/acs.estlett.4c00777>, 2024.](#)
- 710 Lin, M., Horowitz, L. W., Xie, Y., Paulot, F., Malyshev, S., Shevliakova, E., Finco, A., Gerosa, G., Kubistin, D., and Pilegaard, K.: Vegetation feedbacks during drought exacerbate ozone air pollution extremes in Europe, *Nat. Clim. Change*, **10**, 444–451, doi:10.1038/s41558-020-0743-y, 2020.
- Liu, Y. and Wang, T.: Worsening urban ozone pollution in China from 2013 to 2017 – Part 2: the effects of emission changes and implications for multi-pollutant control, *Atmos. Chem. Phys.*, **20**, 6323–6337, doi:10.5194/acp-20-6323-2020, 2020.
- 715 Lu, H., Lyu, X., Cheng, H., Ling, Z., and Guo, H.: Overview on the spatial–temporal characteristics of the ozone formation regime in China, *Environ. Sci.: Processes Impacts*, **21**, 916–929, doi:10.1039/C9EM00047D, 2019.
- Martin, R. V., Fiore, A. M., and van Donkelaar, A.: Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions, *Geophys. Res. Lett.*, **31**, L33102, doi:10.1029/2004GL020939, 2004.

删除了： Li, X., Bei, N., Tie, X., Wu, J., Liu, S., Wang, Q., Zhou, J., Wen, T., Zhang, R., and Li, G.: Local and transboundary transport contributions to the wintertime particulate pollution in the Guanzhong Basin (GZB), China: a case study, *Sci. Total Environ.*, **797**, 148876, doi:10.1016/j.scitotenv.2021.148876, 2021.⁴

- 725 MEE (Ministry of Ecology and Environment): Action Plan for Continuous Improvement of Air Quality, State Council, Beijing, China, https://www.gov.cn/zhengce/content/202312/content_6919000.htm (last access: 09/09/2025), 2023.
- [Mertens, M., Brinkop, S., Graf, P., Grewe, V., Hendricks, J., Lanteri, A., Matthes, S., Rieger, V. S., & Thor, R. N. The contribution of transport emissions to ozone mixing ratios and methane lifetime in 2015 and 2050 in the Shared Socioeconomic Pathways \(SSPs\). *Atmos. Chem. Phys.*, 12079–12106. <https://doi.org/10.5194/acp-24-12079-2024>, 2024.](#)
- 730 Ou, J., Yuan, Z., Zheng, J., Huang, Z., Shao, M., Li, Z., Huang, X., Guo, H., and Louie, P. K. K.: Ambient ozone control in a photochemically active region: short-term despiking or long-term attainment?, *Environ. Sci. Technol.*, 50, 5720–5728, doi:10.1021/acs.est.6b00345, 2016.
- [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.](#)
- 735 Ouyang, B., Ling, Z., Guo, H., Wang, X., Wang, D., Zhou, M., and Wang, B.: Seasonal characteristics and meteorological drivers of ozone pollution in the Pearl River Delta, China, *Atmos. Environ.*, 269, 118856, <https://doi.org/10.1016/j.atmosenv.2021.118856>, 2022.
- Pay, M. T., Gangoiti, G., Guevara, M., Napelenok, S., Querol, X., Jorba, O., and Pérez García-Pando, C.: Ozone source apportionment during peak summer events over southwestern Europe, *Atmos. Chem. Phys.*, 19, 5467–5494, doi:10.5194/acp-19-5467-2019, 2019.
- 740 [Rahman, M. M., Shults, R., and Ali, M. F.: Formaldehyde-to-nitrogen dioxide ratio \(FNR\) analysis for ozone sensitivity: a case study over Bangladesh using OMI data. *Air Qual. Atmos. Health*, 18, 1879–1886. <https://doi.org/10.1007/s11869-025-01732-5>, 2025.](#)
- 745 Ren, S., Wang, Y., Zhang, R., Zhao, Y., Zhang, L., and Wang, X.: Ozone pollution and its precursors in China: trends, drivers, and implications for control, *Environ. Sci. Technol.*, 56, 1794–1804, <https://doi.org/10.1021/acs.est.1c06401>, 2022.
- [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.](#)
- 750 Sillman, S.: The use of NO_y, H₂O₂, and HNO₃ as indicators for ozone–NO_x–hydrocarbon sensitivity in urban locations, *J. Geophys. Res.*, 100, 14175–14188, doi:10.1029/94JD02953, 1995.
- Song, K., Liu, R., Wang, Y., Liu, T., Wei, L., Wu, Y., Shao, M., Zeng, L., and Liu, S. C.: Observation-based analysis of ozone production sensitivity for two persistent ozone episodes in Guangdong, China, *Atmos. Chem. Phys.*, 22, 8403–8416, doi:10.5194/acp-22-8403-2022, 2022.
- 755 [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., Compernelle, S., Pinaridi, G., Vigouroux, C., Langerock, B., Choi, S., Lamsal, L., Zhu, L., Sun, S., Cohen, R. C., Min, K.-E., Cho, C., Philip, S., Liu, X., and Chance, K.: Characterization of errors in satellite-based HCHO/NO₂ tropospheric column ratios with respect to chemistry, column-to-PBL translation, spatial representation, and retrieval uncertainties. *Atmos. Meas. Tech.*, 16, 1961–1986. <https://doi.org/10.5194/amt-16-1961-2023>, 2023.](#)
- 760 State Council: Air Pollution Prevention and Control Action Plan (Guofa (2013) No. 37), Beijing, China, https://www.gov.cn/zwggk/2013-09/12/content_2486773.htm (last access: 05/09/2025), 2013.
- State Council: Three-Year Action Plan for Winning the Blue Sky War (2018–2020), Beijing, China, https://www.gov.cn/zhengce/content/2018-07/03/content_5303154.htm (last access: 05/09/2025), 2018.

- 765 Sun, L., Xue, L., Wang, T., Wang, X., Gao, J., Nie, W., Wang, X., Xu, P., Gao, R., and Wang, Y.: Significant increase of summertime ozone at Mount Tai in Central Eastern China, *Atmos. Chem. Phys.*, 16, 10637–10650, doi:10.5194/acp-16-10637-2016, 2016.
- Sun, Y., Liu, C., Palm, M., Vigouroux, C., Notholt, J., Hu, Q., Liu, J., and Wang, T.: Ozone seasonal evolution and photochemical production regime in the polluted troposphere in eastern China derived from high-resolution Fourier-transform spectrometry observations, *Atmos. Chem. Phys.*, 18, 14569–14583, doi:10.5194/acp-18-14569-2018, 2018.
- 770 Tang, G., Liu, Y., Zhang, J., Liu, B., Li, Q., Sun, J., Wang, Y., Xuan, Y., Li, Y., Pan, J., Li, X., and Wang, Y.: Bypassing the NO_x titration trap in ozone pollution control in Beijing, *Atmos. Res.*, 249, 105333, <https://doi.org/10.1016/j.atmosres.2020.105333>, 2021.
- Wang, J., Gao, J., Che, F., Yang, X., Yang, Y., Liu, L., Li, H., and Wang, T.: Summertime response of ozone and fine particulate matter to mixing-layer meteorology over the North China Plain, *Atmos. Chem. Phys.*, 23, 14715–14733, doi:10.5194/acp-23-14715-2023, 2023.
- 775 Wang, N., Liu, S., Xu, J., Wang, Y., Li, C., Xie, Y., Lu, H., and Yang, F.: Climate-driven biogenic emissions alleviate the impact of human-made emission reductions on O₃ control in the Pearl River Delta region, southern China, *Atmos. Chem. Phys.*, 25, 8859–8870, <https://doi.org/10.5194/acp-25-8859-2025>, 2025.
- Wang, T., Xue, L., Brimblecombe, P., Lam, Y. F., Li, L., and Zhang, L.: Seasonality and reduced nitric oxide titration dominated ozone increases in China, *npj Clim. Atmos. Sci.*, 5, 3, <https://doi.org/10.1038/s41612-021-00222-7>, 2022.
- 780 Wang, R., Bei, N., Tie, X., Wu, J., Liu, S., Li, X., Liu, L., and Li, G.: Effects of hydroperoxy radical heterogeneous loss on the summertime ozone formation in the North China Plain, *Sci. Total Environ.*, 825, 153993, doi:10.1016/j.scitotenv.2022.153993, 2022.
- Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994–2007, *Atmos. Chem. Phys.*, 9, 6217–6227, doi:10.5194/acp-9-6217-2009, 2009.
- 785 Wang, T., Xue, L., Brimblecombe, P., Lam, Y. F., Li, L., and Zhang, L.: Ozone pollution in China: a review of concentrations, meteorological influences, chemical precursors, and effects, *Sci. Total Environ.*, 575, 1582–1596, doi:10.1016/j.scitotenv.2016.10.081, 2017.
- 790 Wang, W., Li, X., Cheng, Y., Parrish, D. D., Ni, R., Tan, Z., Wang, S., Bao, F., and Zhang, Y.: Ozone-pollution mitigation strategy informed by long-term trends of atmospheric oxidation capacity, *Nat. Geosci.*, 17, 20–25, doi:10.1038/s41561-023-01287-7, 2024.
- Wang, W., Parrish, D. D., Wang, S., Bao, F., Ni, R., Li, X., Wu, X., Feng, X., Zhang, F., and Su, H.: Long-term trend of ozone pollution in China during 2014–2020: distinct seasonal and spatial characteristics and ozone sensitivity, *Atmos. Chem. Phys.*, 22, 8935–8949, doi:10.5194/acp-22-8935-2022, 2022.
- 795 Wang, X., Fu, T. M., Zhang, L., Cao, H., Zhang, Q., Ma, H., Zhao, B., and Henze, D. K.: Sensitivities of ozone air pollution in the Beijing–Tianjin–Hebei area to local and upwind precursor emissions using adjoint modeling, *Environ. Sci. Technol.*, 55, 5752–5762, doi:10.1021/acs.est.0c08167, 2021.
- 800 Wang, Y., Zhao, Y., Liu, Y., Jiang, Y., Zheng, B., Xing, J., Wang, S., Zhang, L., and Nielsen, C. P.: Sustained emission reductions have restrained the ozone pollution over China, *Nat. Geosci.*, 16, 967–974, doi:10.1038/s41561-023-01284-w, 2023.
- 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.

- 805 Wu, J., Bei, N., Hu, B., Liu, S., Zhou, M., Wang, Q., Li, X., Liu, L., Wang, R., Shen, Z., and Li, G.: Is water vapor a key player of the wintertime haze in North China Plain?, *Atmos. Chem. Phys.*, 19, 8721–8739, doi:10.5194/acp-19-8721-2019, 2019.
- Wu, J., Bei, N., Hu, B., Liu, S., Wang, Y., Shen, Z., Li, X., Liu, L., Wang, R., Liu, Z., and Li, G.: Aerosol–photolysis interaction reduces particulate matter during wintertime haze events, *Proc. Natl. Acad. Sci. USA*, 117, 9755–9761, doi:10.1073/pnas.1919728117, 2020a.
- 810 Wu, K., Yang, X., Chen, D., Gu, S., Lu, Y., Jiang, Q., Bi, X., Wang, X., Li, Z., and Lu, S.: Estimation of biogenic VOC emissions and their corresponding impact on ozone and secondary organic aerosol formation in China, *Atmos. Res.*, 231, 104656, <https://doi.org/10.1016/j.atmosres.2019.104656>, 2020b.
- Wu, R. and Xie, S.: Spatial distribution of ozone formation in China derived from emissions of speciated volatile organic compounds, *Environ. Sci. Technol.*, 51, 2574–2583, doi:10.1021/acs.est.6b05401, 2017.
- 815 Xiao, Q., Geng, G., Xue, T., Liu, S., Cai, C., He, K., and Zhang, Q.: Tracking PM_{2.5} and O₃ pollution and the related health burden in China 2013–2020, *Environ. Sci. Technol.*, 56, 6922–6932, doi:10.1021/acs.est.1c08835, 2022.
- Xu, D., Yuan, Z., Wang, M., Zhao, K., Liu, X., Duan, Y., and Zhao, X.: Multi-factor reconciliation of discrepancies in ozone-precursor sensitivity retrieved from observation- and emission-based models, *Environ. Int.*, 158, 106952, doi:10.1016/j.envint.2021.106952, 2022.
- 820 Xu, W., Lin, W., Xu, X., Tang, J., Huang, K., Gao, W., and Zhang, G.: Long-term trends of surface ozone and its influencing factors at the Mt. Waliguan GAW station, China – Part I: overall trends and characteristics, *Atmos. Chem. Phys.*, 16, 6191–6205, doi:10.5194/acp-16-6191-2016, 2016.
- Xu, W., Wang, T., Xue, L., Louie, P. K. K., Luk, C. W. Y., Gao, J., Wang, S., Chai, F., Wang, W., and Wang, X.: Long-term measurements of surface ozone and its precursors in the Yangtze River Delta, China: characteristics, trends, and meteorological influences, *Sci. Total Environ.*, 699, 134236, <https://doi.org/10.1016/j.scitotenv.2019.134236>, 2020.
- 825 [Ye, X., Yang, J., Wang, R., Sun, J., Liu, Z., Chen, Z., Li, G., and Shen, Z.: From sensitivity regimes to policy action: Evaluating EKMA curve effectiveness with WRF-Chem, OBM, and machine learning, *Atmos. Environ.*, \[Volume/Pages 待补充\], doi:10.1016/j.atmosenv.2025.121689, 2025.](#)
- 830 Yu, H., Chang, Y., Cheng, L., Duan, Y., and Hu, J.: Measurement report: Long-term assessment of primary and secondary organic aerosols in the Shanghai megacity throughout China's Clean Air actions since 2010, *Atmos. Chem. Phys.*, 25, 5355–5369, <https://doi.org/10.5194/acp-25-5355-2025>, 2025.
- Yu, X., Zhao, B., Chen, Y., Li, J., Wang, S., and Wu, J.: Diagnosing ozone formation regimes and optimal precursor reduction ratios in Zhengzhou, China, *Atmos. Environ.*, 319, 120218, <https://doi.org/10.1016/j.atmosenv.2025.120218>, 2025.
- 835 Zhang, Q., Zheng, Y., Tong, D., Shao, M., Wang, S., Zhang, Y., Xu, X., Wang, J., He, H., Liu, W., Ding, Y., Lei, Y., Li, J., Wang, Z., Zhang, X., Wang, Y., Cheng, J., Liu, Y., Shi, Q., Yan, L., Geng, G., Hong, C., Li, M., Liu, F., Zheng, B., Cao, J., Ding, A., Gao, J., Fu, Q., Huo, J., Liu, B., Liu, Z., Yang, F., He, K., and Hao, J.: Drivers of improved PM_{2.5} air quality in China from 2013 to 2017, *Proc. Natl. Acad. Sci. USA*, 116, 24463–24469, doi:10.1073/pnas.1907956116, 2019.
- [Zhao, C., Sun, Y., Yang, J., Li, J., Zhou, Y., Yang, Y., Fan, H., and Zhao, X.: Decadal evolution of aerosol-mediated ozone responses in Eastern China under clean-air actions and carbon-neutrality policies, *Atmos. Chem. Phys.*, 26, 1301–1318, <https://doi.org/10.5194/acp-26-1301-2026>, 2026.](#)
- 840 Zhao, M., Zhang, Y., Pei, C., Chen, T., Mu, J., Liu, Y., Wang, Y., and Xue, L.: Worsening ozone air pollution with reduced NO_x and VOCs in the Pearl River Delta region in autumn 2019: implications for national control policy in China, *J. Environ. Manage.*, 324, 116327, <https://doi.org/10.1016/j.jenvman.2022.116327>, 2022.

Zhao, X., Tian, W., and Chen, D.: Impacts of thermal power industry emissions on air quality in China, *Sustainability*, 17, 441, <https://doi.org/10.3390/su17020441>, 2025.

845 Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi, J., Yan, L., Zhang, Y., Zhao, H., Zheng, Y., He, K., and Zhang, Q.: Trends in China's anthropogenic emissions since 2010 as the consequence of clean air actions, *Atmos. Chem. Phys.*, 18, 14095–14111, doi:10.5194/acp-18-14095-2018, 2018.

Zhu, S., Liu, Y., Xie, Y., Ren, J., Cheng, H., and Shen, L.: Shifts of formation regimes and increases of atmospheric oxidation led to ozone increase in North China Plain and Yangtze River Delta from 2016 to 2019, *J. Geophys. Res. Atmos.*, 127, e2022JD038373, <https://doi.org/10.1029/2022JD038373>, 2022.

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Table 1: Warm-season exceedance frequency and mean concentration of MDA8 O₃ in the GZB and its Cities from 2014 to 2024.

	Exceedance frequency						the Mean concentration ($\mu\text{g m}^{-3}$)					
	XA	XY	WN	TC	BJ	GZB	XA	XY	WN	TC	BJ	GZB
2014	9.8%	8.5%	5.7%	12.6%	5.0%	8.3%	175.3	186.7	182.2	183.2	178.0	179.0
2015	14.3%	8.1%	7.1%	12.2%	6.1%	10.4%	179.3	176.0	177.0	175.5	178.8	178.1
2016	22.4%	26.8%	23.8%	28.0%	16.5%	22.3%	190	187.2	179.6	178.0	175.0	183.3
2017	43.1%	49.2%	43.3%	30.5%	19.7%	36.7%	194.6	199.5	186.7	184.5	171.2	188.8
2018	31.3%	38.5%	30.7%	27.2%	11.6%	26.5%	190.6	201.7	179.4	181.7	172.1	184.5
2019	25.2%	24.1%	26.8%	20.7%	3.7%	19.4%	183.6	178.1	176.9	174.7	171.3	178.1
2020	17.1%	17.9%	13.4%	13.6%	6.3%	13.6%	185.7	179.7	176.9	182.6	178.3	181.8
2021	20.9%	24.7%	25.2%	17.3%	8.3%	18.2%	194.8	188.5	187.5	179.7	173.2	185.9
2022	34.1%	41.5%	22.8%	16.8%	15.9%	26.7%	185.5	181.7	179.7	176.5	174.9	180.6
2023	32.7%	34.1%	17.9%	16.5%	13.4%	23.7%	187.2	185.7	183.4	177.7	174.2	182.0
2024	33.8%	42.3%	27.9%	20.7%	14.0%	27.0%	180.6	184.7	176.4	174.1	174.5	178.2

Table 2: MDA8 O₃ contribution of various sources in urban areas of the GZB and five cities during warm season in 2022.

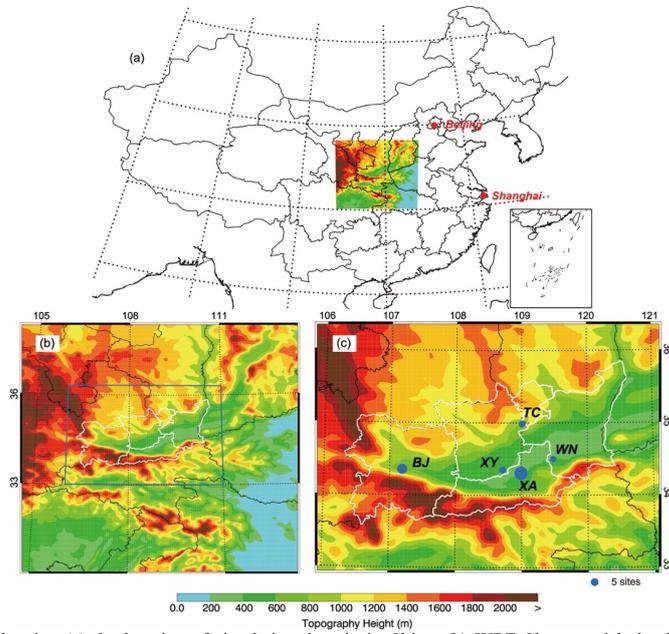
Month	Region	Anthro	Bio	Ind	Pow	Tra	Res
May	GZB	32.77%	9.74%	5.41%	-4.39%	5.81%	3.30%
	XA	37.14%	10.46%	6.43%	-2.40%	5.02%	3.92%
	XY	35.69%	10.73%	4.64%	-3.59%	4.77%	3.16%
	WN	13.95%	9.05%	5.84%	-21.82%	7.59%	3.32%
	TC	29.80%	8.90%	1.22%	0.32%	7.07%	2.36%
	BJ	29.32%	7.13%	4.13%	-0.89%	7.93%	1.99%
June	GZB	47.92%	11.52%	14.39%	1.29%	13.61%	4.07%
	XA	52.71%	11.71%	17.44%	3.56%	13.41%	4.89%
	XY	52.67%	11.23%	14.31%	3.99%	14.56%	4.11%
	WN	27.44%	11.85%	10.90%	-18.17%	13.42%	3.16%
	TC	42.58%	11.92%	6.27%	5.87%	13.48%	2.97%
	BJ	39.96%	11.08%	8.95%	1.60%	12.93%	2.28%
July	GZB	55.23%	18.67%	11.80%	3.67%	16.95%	3.11%
	XA	58.74%	18.97%	13.15%	6.26%	16.76%	2.80%
	XY	59.21%	19.89%	12.11%	6.70%	17.04%	4.18%
	WN	34.69%	16.61%	9.40%	-18.13%	15.49%	2.61%
	TC	51.43%	19.44%	5.86%	9.28%	15.91%	2.30%
	BJ	52.11%	17.15%	10.00%	3.54%	18.34%	2.89%
August	GZB	47.97%	16.73%	10.44%	3.08%	15.74%	2.57%
	XA	51.09%	16.45%	11.01%	4.41%	15.44%	2.35%
	XY	52.33%	18.14%	11.08%	5.61%	16.21%	2.31%
	WN	34.63%	18.46%	10.62%	-9.05%	15.91%	2.55%
	TC	41.73%	15.87%	3.45%	7.37%	14.45%	1.85%
	BJ	43.35%	14.48%	9.04%	3.32%	16.00%	3.67%

Note: XA, XY, WN, BJ, TC and GZB represent the urban areas in Xi'an, Xianyang, Weinan, Baoji, Tongchuan and the Guanzhong Basin respectively. Anthro, Ind, Tra, Pow, Res, and Bio represent total anthropogenic, industry, traffic, power plants, residential, and biogenic source, respectively.

Table 3: SA contribution of various sources in urban areas of the GZB and five cities during warm season in 2022.

Month	Region	Anthro	Bio	Ind	Pow	Tra	Res
May	GZB	78.79%	3.16%	19.78%	17.28%	23.90%	15.69%
	XA	80.04%	4.07%	21.12%	16.09%	23.90%	16.59%
	XY	80.19%	3.38%	18.10%	16.44%	25.08%	16.09%
	WN	74.98%	1.53%	15.65%	25.56%	17.46%	10.33%
	TC	74.60%	0.11%	19.11%	16.18%	24.07%	13.95%
	BJ	76.82%	1.97%	21.86%	15.58%	27.33%	17.08%
June	GZB	74.93%	4.30%	21.10%	15.96%	29.22%	19.80%
	XA	76.56%	4.20%	24.97%	13.84%	31.05%	20.93%
	XY	75.94%	4.41%	19.22%	14.43%	32.86%	21.43%
	WN	75.10%	3.42%	15.12%	31.38%	18.39%	12.37%
	TC	70.29%	1.83%	16.73%	14.00%	26.89%	19.06%
	BJ	68.67%	5.75%	17.67%	11.30%	28.02%	20.65%
July	GZB	85.42%	2.31%	25.34%	26.65%	31.75%	14.21%
	XA	85.41%	2.67%	26.56%	23.26%	32.77%	14.88%
	XY	85.96%	2.46%	23.41%	27.42%	34.85%	15.72%
	WN	86.48%	2.61%	24.49%	40.33%	21.71%	7.07%
	TC	82.43%	-0.16%	24.91%	27.66%	30.61%	14.63%
	BJ	84.15%	1.15%	25.57%	21.79%	34.15%	16.86%
August	GZB	69.71%	6.58%	20.01%	18.98%	22.05%	14.28%
	XA	69.12%	8.42%	21.03%	15.25%	22.88%	15.52%
	XY	70.00%	8.50%	18.43%	18.06%	24.36%	14.70%
	WN	74.76%	3.83%	21.09%	33.74%	16.44%	9.71%
	TC	63.98%	1.75%	15.38%	15.63%	20.15%	11.55%
	BJ	66.20%	2.89%	19.13%	14.28%	23.14%	15.98%

Note: XA, XY, WN, BJ, TC and GZB represent the urban areas in Xi'an, Xianyang, Weinan, Baoji, Tongchuan and the Guanzhong Basin respectively. Anthro, Ind, Tra, Pow, Res, and Bio represent total anthropogenic, industry, traffic, power plants, residential, and biogenic source, respectively.



875 **Figure 1:** Map showing (a) the location of simulation domain in China, (b) WRF-Chem model simulation domain with topography. In (c), the filled blue circles represent centers of cities with ambient monitoring sites and the size of circles denotes the number of ambient monitoring sites of cities. The white boundary outlines the Guanzhong Basin (GZB), the focus region of this study, comprising five cities: Xian (XA), Xianyang (XY), Weinan (WN), Tongchuan (TC), and Baoji (BJ).

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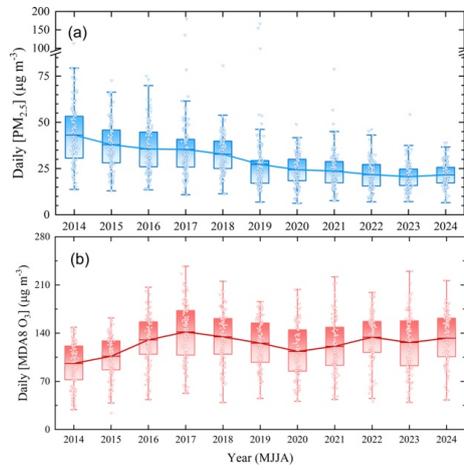
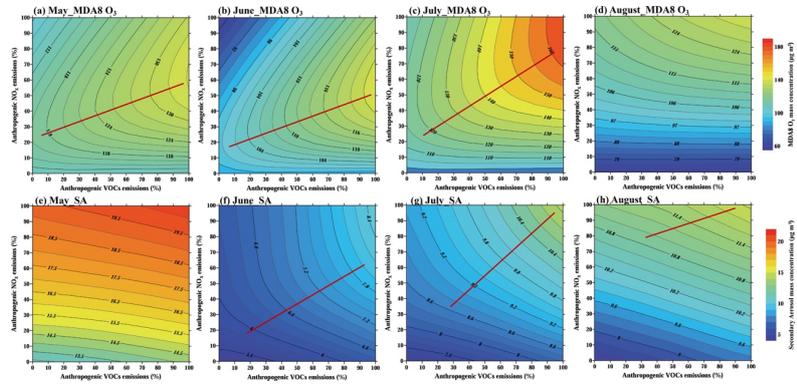


Figure 2: Interannual variations of the warm-season (May–August) mean (a) PM_{2.5} and (b) MDA8 O₃ concentrations in the GZB during 2014–2024, based on observations from 33 national monitoring sites. Box plots show the distribution (25th–75th percentiles, mean, whiskers, and outliers), and solid connecting lines indicate annual means, highlighting long-term trends.

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Figure 3: MDA8 O₃ & SA isopleth profiles ($\mu\text{g m}^{-3}$) in urban areas of the GZB in high-O₃ pollution episode during (a) & (e) May, (b) & (f) June, (c) & (g) July, (d) & (h) August 2022. The VOC-limited and NO_x-limited regimes are separated by the red ridge lines. (d) and (e) indicate the formation regime in the GZB are NO_x-limited with no red ridge lines displayed in the isopleth at current emission mitigation scenarios.

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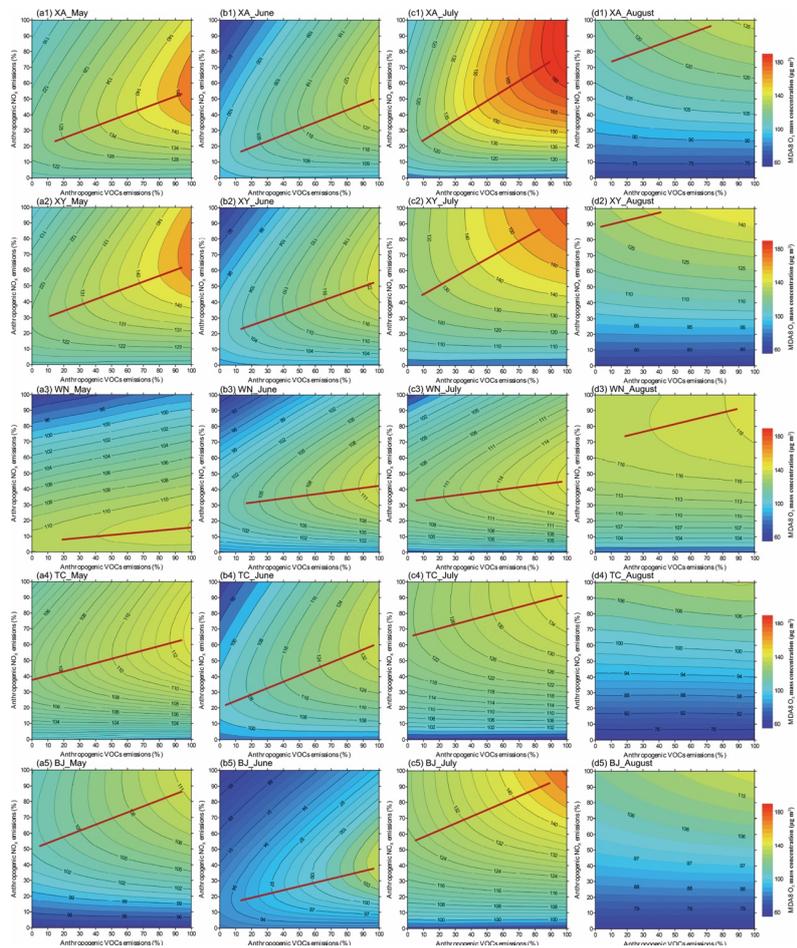


Figure 4: MDA8 O₃ isopleth profiles ($\mu\text{g m}^{-3}$) in urban areas of (*1) XA, (*2) XY, (*3) WN, (*4) TC, and (*5) BJ in high-O₃ pollution episode during (a*) May, (b*) June, (c*) July, (d*) August 2022. The VOCs-limited and NO_x-limited regimes are separated by the red ridge lines. (d4) and (d5) indicate the formation regime are NO_x-limited with no red ridge lines displayed in the isopleth at current emission mitigation scenarios.

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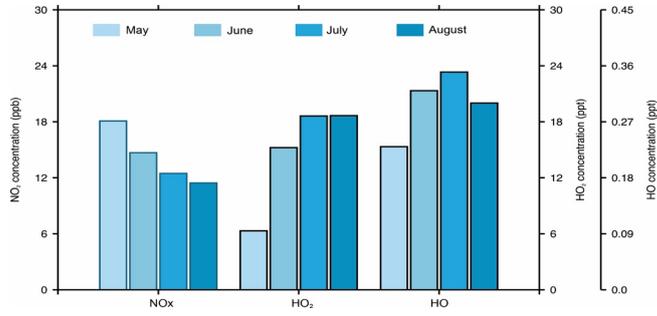
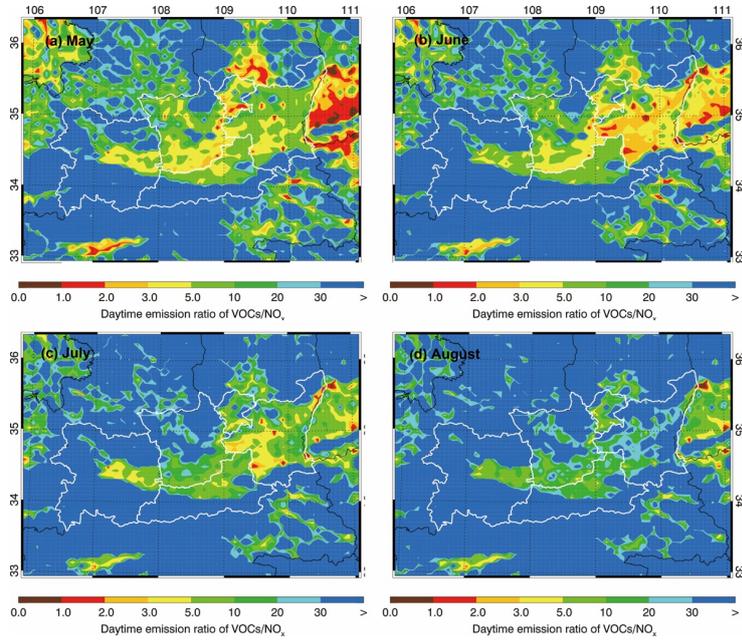
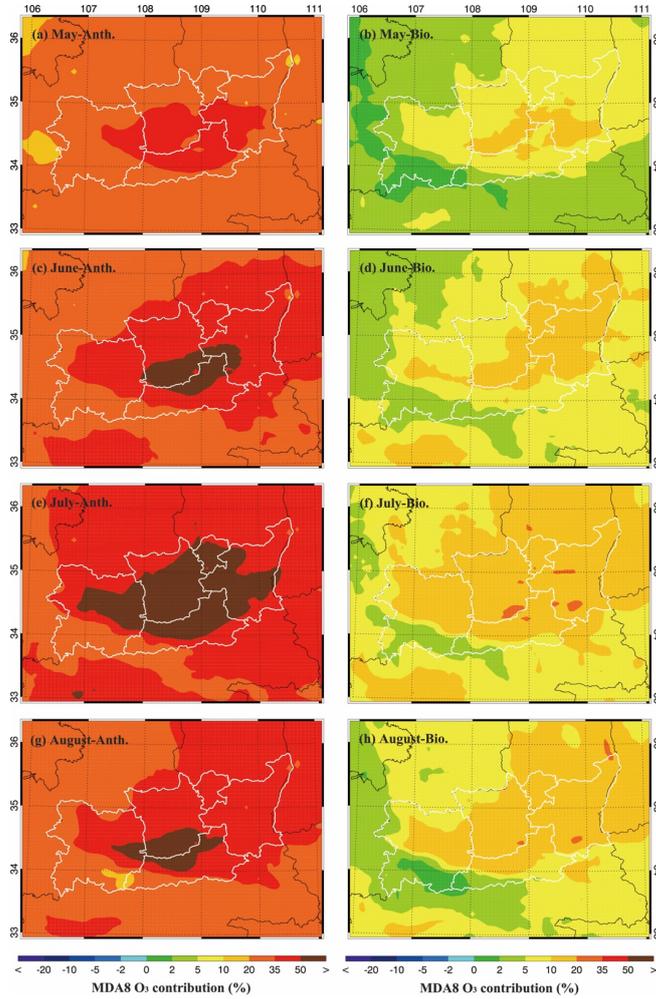


Figure 5: The mean daytime (08:00 – 20:00 BJT) NO_x, HO₂ and HO concentrations from May to August 2022 in urban areas of the GZB.



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Figure 6: The spatial distribution of total VOCs (includes BVOCs and AVOCs) to NO_x emission ratios in (a) May, (b) June, (c) July and (d) August 2022.



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Figure 7: The spatial distribution of the mean MDA8 O₃ contribution from (a) & (c) & (e) & (g) total anthropogenic, and (b) & (d) & (f) & (h) biogenic sources from May to August 2022.

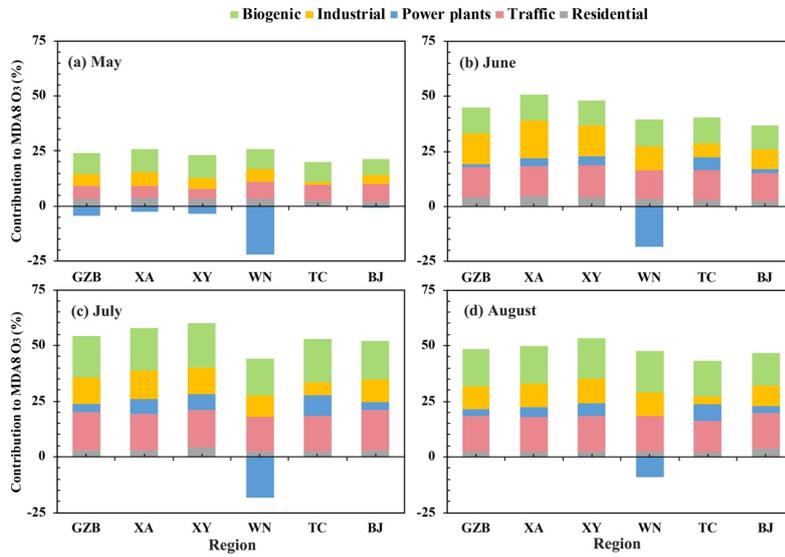
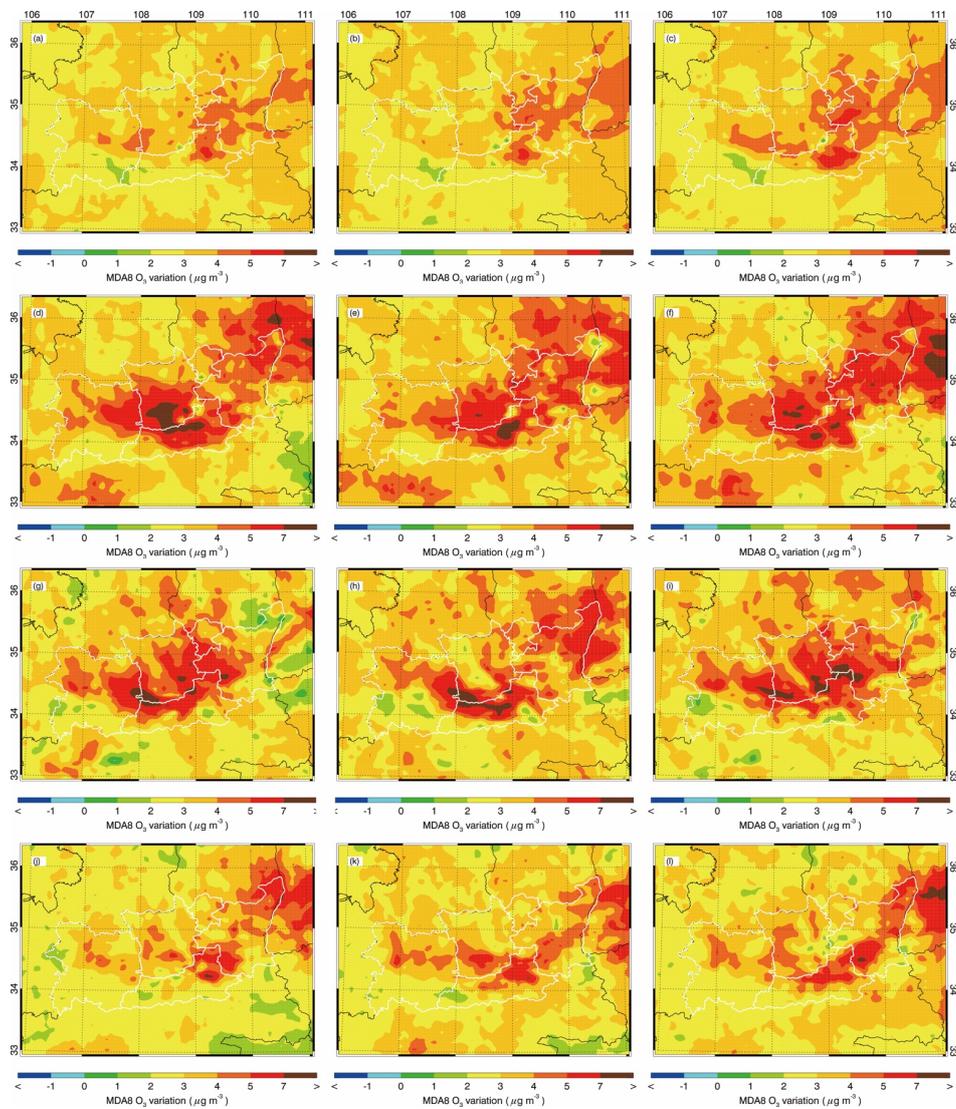


Figure 8: Mean MDA8 O₃ contributions from various sources in (a) May, (b) June, (c) July, and (d) August 2022 in urban areas of the GZB and five cities.

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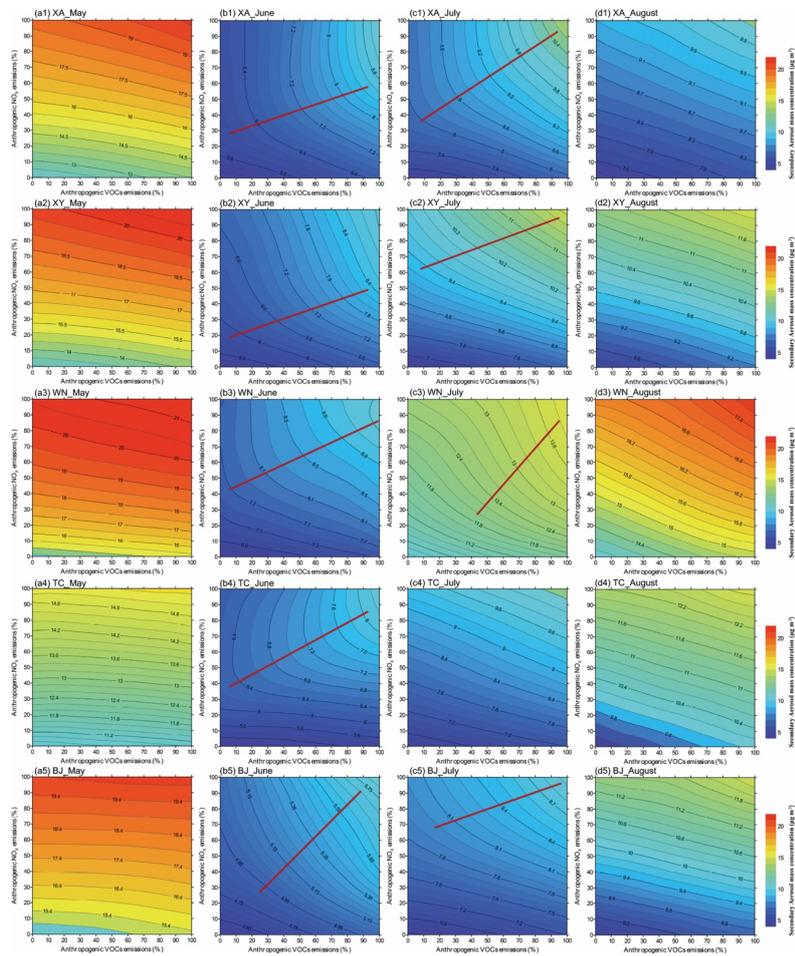
925 **Figure 9:** Impacts of aerosol changes on warm-season (May–August) MDA8 O₃ concentrations over the GZB during 2014–2022. Panels (a), (d), (g), and (j) show the changes in MDA8 O₃ attributable to aerosol-radiation effects associated with aerosol variations for May, June, July, and August, respectively. Panels (b), (e), (h), and (k) show the corresponding MDA8 O₃ changes driven by variations in heterogeneous uptake of HO₂ radicals on wet aerosol surfaces induced by aerosol changes. Panels (c), (f), (i), and (l) present the combined effects of aerosol-radiation interactions and HO₂ heterogeneous uptake changes on MDA8 O₃ concentrations for the corresponding months.

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35 **Figure 10:** SA isopleth profiles ($\mu\text{g m}^{-3}$) in urban areas of (*1) XA, (*2) XY, (*3) WN, (*4) TC, and (*5) BJ in high- O_3 pollution episode during (a*) May, (b*) June, (c*) July, (d*) August 2022. The VOCs-limited and NO_x -limited regimes are separated by the red ridge lines. (a*), (c4) and (d*) indicate the formation regime are NO_x -limited with no red ridge lines displayed in the isopleth at current emission mitigation scenarios.

