We sincerely thank the reviewers for their careful and constructive comments. All comments have been thoroughly considered and addressed in the revised manuscript. Below, we provide point-by-point responses. The authors' responses are indicated in blue, and all changes made to the manuscript are highlighted in red.

Reviewer #1:

Overview

This study showed how ozone formation sensitivity changes diurnally in urban areas using GEMS satellite data over China in the warm season from 2021-2023. It was found that NO_2 generally decreased throughout the day, and both HCHO and ozone increased. The diurnal variations of ozone formation are also affected by local meteorology that may enhance or inhibit the ozone formation reactions, leading to differences in different cities, suggesting the need for city- and time-specific emission controls.

This paper uses a novel dataset with the GEMS satellite data, and I recommend this manuscript for publication after the following revisions.

General Comments

1. The temporal extent of the study was not clearly defined in the text. Additionally, justifications for the temporal extent would be beneficial. For example, why was 2021-2023 used for the study, what is the definition of the warm season, and why was only the warm season investigated? References to the study period also seemed inconsistent throughout the text.

Response: We thank the reviewer for raising this important point. The study period was not sufficiently clear in the original manuscript. We have now systematically clarified and unified the temporal definition throughout the paper, as detailed below.

(1) Why 2021–2023?

The GEMS hourly products have been operationally stable and fully validated since 2021. We therefore focus on 2021–2023 to ensure data quality and multi-year comparability. This justification has been added to the Introduction (lines 141–143), citing Lange et al., 2024 and Bae et al., 2025.

(2) Definition of "warm season" and why only warm season?

Following common practice in Chinese ozone research, we define the warm season as April–September, when high temperature and strong solar radiation drive active photochemistry and severe ozone pollution (Guicai et al., 2022). This clarification has been added to the Introduction (lines 143–146).

(3) Consistency of temporal expressions across figures

We have unified the study period description in the abstract, main text, and figure captions. Specifically:

1)All analyses are based on hourly data from 09:00–16:00 LST during April–September, 2021–2023.

2)Figure 7 shows the diurnal characteristics for 2023 only (the most recent year), while Figure 8 shows the same for 2021–2022 to illustrate interannual continuity.

3)Figure 9 uses the full 2021–2023 average for representative cities.
These choices are explicitly stated in the respective figure captions and do not create inconsistency. The revised temporal descriptions have been added to the Abstract (lines 18–21) and Figure 9 caption (lines 508–509).

2. The use of TROPOMI data to compare to GEMS would be much more beneficial for the community if they were quantitatively and statistically compared. For example, Figure 5 shows that there are clear discrepancies between the two sensors for the NO_2 and HCHO products. Doing a statistical analysis to quantify the spatial agreement and differences between NO_2, HCHO, and FNRs would be more impactful. Additionally, the use of TROPOMI data should also be mentioned in Section 2 alongside the GEMS data.

Response: We thank the reviewer for this constructive suggestion. We agree that a quantitative comparison between GEMS and TROPOMI is essential. Accordingly, we have:

(1)Added TROPOMI data description in Section 2 (now lines 196–207), including data period, quality control (qa_value > 0.75), retrieval method (DOAS), and spatial resolution.
(2)Performed statistical analyses (Pearson's r, mean bias, linear regression) for HCHO, NO_2, and FNR between the two sensors, presented in new Supplementary Fig. S5 and described in lines 344–356.

Key results:
1)NO_2 shows good agreement (r = 0.838, MB = -2.509×10^{15} molec cm^{-2}), consistent with previous validation studies (Lee et al., 2024; Kim and Kim, 2023).
2)HCHO exhibits moderate correlation (r = 0.506, MB = 0.185×10^{15} molec cm^{-2}). This relatively lower agreement likely reflects known challenges in HCHO retrievals (lower signal-to-noise ratio, stronger influence of a priori profiles) and the different overpass times (GEMS: hourly daytime; TROPOMI: ~13:30 local time). We have noted this in the revised manuscript.
3)FNR, as a ratio, partially cancels systematic biases and shows strong agreement (r = 0.783, MB = 1.172), supporting the robustness of our ozone regime classification.

We also note that the discrepancies visible in original Figure 5 are largely attributable to the different overpass times and spatial sampling. The added quantitative analysis (Fig. S5) provides a more rigorous basis for interpreting these differences. We believe these revisions address the reviewer's concern.

3. Generally, all discussions of results could generally benefit from additional quantitative comparisons, especially including statistical support for the relationships between variables.
Response: We thank the reviewer for this important suggestion. In the revised

manuscript, we have substantially strengthened quantitative comparisons and statistical support across multiple sections, as detailed below:

(1) Pollutant–meteorology relationships (Section 3.1, lines 255–278; new Table S1; new Figs. S1–S4)

We added hourly spatial maps of T_{2m}, RH, SSR, and BLH, and performed Spearman correlation analysis between O_3, HCHO, NO_2 and these meteorological variables. Key findings:

1)HCHO is significantly positively correlated with T_2m ($\rho = 0.531$, $p < 0.01$) and SSR ($\rho = 0.415$, $p < 0.01$).

2)NO_2 is significantly negatively correlated with T_2m ($\rho = -0.556$, $p < 0.01$) and BLH ($\rho = -0.201$, $p < 0.01$).

These results quantitatively support the photochemical drivers of diurnal variations.

(2) GEMS vs. TROPOMI inter-sensor comparison (Section 3.2, lines 344–356; new Fig. S5)

As detailed in our response to the second comment, we added Pearson correlation and mean bias analyses for HCHO, NO_2, and FNR. The FNR shows strong agreement ($r = 0.783$), supporting the robustness of our ozone regime classification.

(3) LOESS-based ozone sensitivity classification with bootstrap uncertainty (Section 3.2, lines 357–379)

To quantitatively define the VOC-limited, transitional, and NO_x-limited regimes, we applied LOESS regression to the O_3–FNR relationship and used bootstrap resampling (1000 iterations) to estimate the 95% confidence interval of the fitted curve. This provides statistical rigor to the regime classification and allows for quantitative uncertainty assessment.

We believe these additions comprehensively address the reviewer's concern regarding quantitative support for the results.

Specific Comments

1. Lines 44-46: In general, how were the ozone sensitivity classes defined for your study? This was not clearly discussed in the paper.

Response: We thank the reviewer for pointing out this lack of clarity. In the revised manuscript, we have added a detailed description of how the ozone sensitivity classes (VOC-limited, transitional, NO_x-limited) are defined. The following text has been added to the Methods section (lines 231–244):

"This study employs locally estimated scatterplot smoothing (LOESS) to characterize the nonlinear relationship between O_3 and FNR. LOESS is a nonparametric regression method that fits low-order polynomials to localized subsets of data, requiring no predetermined global functional form. Specifically, hourly O_3 concentrations and their corresponding FNR values were fitted to obtain the functional relationship $O_3 = f(FNR)$.

To identify high-response regions for ozone formation, the peak of the LOESS curve (denoted as f_max) was first determined. The FNR interval satisfying $f(FNR)$

≥ 0.9 × f_max was then defined as the transitional (high-response) regime. Based on the endpoints of this interval (FNR_start and FNR_end), ozone formation sensitivity was classified into three regimes:
VOC-limited: FNR < FNR_start
Transitional: FNR_start ≤ FNR ≤ FNR_end
NO_x-limited: FNR > FNR_end

To assess the robustness of the fit, a bootstrap approach with 1000 resamples was applied to estimate the 95% confidence interval of the LOESS curve."
This definition is consistently applied throughout the analysis. We believe this revision fully addresses the reviewer's concern.

2. Lines 87-103: the literature discussed here shows how ozone sensitivity changes for spring, summer, and autumn, but not the winter, which would explain the full cycle of seasonal variations in ozone formation. How does ozone sensitivity change in the winter?

Response: We thank the reviewer for this important observation. The original manuscript indeed focused on spring, summer, and autumn without explicitly discussing winter. We have now added a discussion of winter ozone sensitivity in the revised manuscript (lines 97–100), as summarized below:
"At seasonal and monthly scales, ozone sensitivity also shows systematic variations; for example, under high-temperature and strong-radiation conditions in summer, NO_x-limited or transitional regimes are more prevalent, whereas VOC-limited regimes tend to dominate in spring and autumn and winter. (Li, 2023; Yin et al., 2024)."
We believe this addition directly addresses the reviewer's question regarding winter ozone sensitivity.

3. Line 163: is the purpose of Figure 1a-b just to show the first and last available scans for each day over the study area? Why is this important for the paper?

Response: We thank the reviewer for this question. We have clarified the purpose and importance of Figure 1a–b in the revised manuscript (lines 187–190).
The figure serves two purposes:
（1）To show the temporal coverage of GEMS: GEMS covers most of China from 08:45 to 15:45 LST at hourly intervals, defining the exact time window available for our diurnal analysis.
（2）To justify the 09:00–16:00 analysis period: By showing the first and last daily overpasses, the figure demonstrates that our analysis window (09:00–16:00) falls fully within GEMS's observational coverage, ensuring that all hourly data points are valid and complete.

This is important because unlike polar-orbiting satellites (e.g., TROPOMI) that provide only one overpasses per day, GEMS enables hourly diurnal analysis, but only within a fixed daily window. Figure 1a–b makes this window explicit and transparent to the

reader. We have added this justification in the revised manuscript.

4. Line 168-169: what retrieval algorithms are used for the GEMS L2 HCHO and NO_2 products? A brief description of the retrieval algorithms used may be helpful for readers.

Response: We thank the reviewer for this suggestion. A brief description of the retrieval algorithms for GEMS L2 HCHO and NO_2 products has been added to the Data and Methods section (lines 180–187 in the revised version), as follows:
"The GEMS L2 HCHO and NO_2 products are retrieved using the Differential Optical Absorption Spectroscopy (DOAS) method. First, the slant column densities (SCDs) of the target gases are obtained through DOAS fitting of the ultraviolet–visible spectra. The SCDs are then converted to tropospheric vertical column densities (VCDs) by applying air mass factors (AMFs) derived from a radiative transfer model. The main sources of uncertainty include spectral fitting errors, AMF calculation errors, and assumptions in the a priori profiles. Detailed retrieval principles and product validation can be found in Kim et al. (2020) and Lange et al. (2024)."

We believe this addition provides readers with sufficient background on the retrieval methodology without overburdening the main text.

5. Lines 183-185: how were the gridded GEMS data compared to the point station data?

Response: We thank the reviewer for this question. As described in the revised manuscript (lines 219–223), we used a KDTree nearest-neighbor approach to match ground stations to their nearest GEMS grid points, following the approach of previous studies (Souri et al., 2023). This provides a clear spatial correspondence between gridded satellite data and point station observations.

6. Lines 208-210: it is difficult to distinguish between which panels contain the HCHO and NO_2 data in Figure 2.

Response: We thank the reviewer for pointing out this issue. The figure legend for Figure 2 has been revised in the manuscript (see line 307) to clearly distinguish between HCHO and NO_2 panels. Specifically, the original legend"HCHO and NO_2 (10^{15} molec cm^{-2})" has been changed to "(a–h) HCHO and (i–p) NO_2 (10^{15} molec cm^{-2})". With this revision, readers can now easily identify which panels correspond to which species.

7. Lines 225-230: how do the meteorological variables vary spatially in the study region? Something similar to Figure 2 may be helpful for showing the spatiotemporal variations in meteorology. Additionally, are the temporal variations between the pollutants and meteorology correlated or statistically significant?

Response: We thank the reviewer for these two important questions. We have addressed them as follows:

(1) Spatial variations of meteorological variables

To show how meteorological variables vary spatially (similar to Figure 2), we have added hourly spatial distribution maps of T_{2m}, RH, SSR, and BLH in the Supplementary Material (Figs. S1–S4; see lines 255–258 in the revised manuscript). These maps indicate that the BTH, YRD, PRD, and SC regions generally exhibit higher T_2m, SSR, and BLH, providing favorable conditions for photochemical reactions.

(2) Statistical significance of pollutant–meteorology relationships

As detailed in our response to the previous comment (General Comment #3) and presented in Table S1 (lines 258–262, 274–276), we performed Spearman correlation analysis and found statistically significant correlations ($p < 0.01$) between pollutants (HCHO, NO_2) and meteorological variables (T_{2m}, SSR, BLH). The results confirm that the temporal variations are both correlated and statistically significant.

8. Line 287: which TROPOMI HCHO/NO_2 data were used and how different is the retrieval process compared to GEMS? The use of TROPOMI data was not mentioned in Section 2 (Data and Methods).

Response: We thank the reviewer for these questions. We have added the TROPOMI data description to Section 2.1 (lines 196–207). Below we address the two specific questions:

(1) Which TROPOMI HCHO/NO_2 data were used?

We used tropospheric HCHO and NO_2 column data from the Sentinel-5P TROPOMI OFFL L3 products for 2021–2023, obtained via the Google Earth Engine platform. Data were filtered using qa_value > 0.75 to remove cloud contamination and low-quality observations.

(2) How different is the retrieval process compared to GEMS?

Both TROPOMI and GEMS retrieve gas column densities using the DOAS method in the UV–vis range, so the fundamental principles are similar. However, key differences include:

1)Orbit and temporal resolution: TROPOMI is polar-orbiting (~1 overpass/day), while GEMS is geostationary (hourly observations).

2)Retrieval details: Although both use DOAS, differences exist in spectral fitting windows, reference spectra, and air mass factor calculations due to different instrument designs and observation geometries. Detailed comparisons can be found in Kim et al. (2020) and Lange et al. (2024).

In this study, TROPOMI data are primarily used for validation and spatial comparison, while GEMS data support the diurnal analysis. We have also noted that TROPOMI NO_2 shows high correlation (R=0.9) with GEMS NO_2 (Oak et al., 2024), confirming its reliability.

9. Lines 287-292: what is the statistical relationship between the NO_2, HCHO, and FNR values for GEMS and TROPOMI for your study? Including some quantitative and statistical parameters such as correlations and discrepancies should be included. Additionally, have discrepancies between the HCHO and NO_2 data products been previously discussed in the literature?

Response: We thank the reviewer for these two important questions. We have added a quantitative comparison between GEMS and TROPOMI in the revised manuscript (Supplementary Fig. S5; lines 344–356). Below we address each question separately.

(1) Statistical relationship between GEMS and TROPOMI (NO_2, HCHO, and FNR)

As detailed in our responses to the previous comments (General Comments #2 and #3), we calculated Pearson correlation coefficients (r) and mean bias (MB) for HCHO, NO_2, and FNR. The results are presented in Supplementary Fig. S5. In brief, the FNR shows strong agreement (r=0.783), supporting the robustness of our ozone regime classification.

(2) Have discrepancies between HCHO and NO_2 products been previously discussed in the literature?

Yes. Previous studies have compared GEMS and TROPOMI HCHO/NO_2 products and discussed their discrepancies. For example, Fu et al. (2024) and He (2025) reported correlation coefficients ranging from 0.59 to 0.85, with differences within 20% in most regions. These discrepancies are primarily attributed to differences in orbital configuration (geostationary vs. polar-orbiting), overpass time, spatial resolution, and retrieval assumptions (e.g., spectral fitting windows, AMF calculations). We have cited these studies in the revised manuscript (see lines 353–356) to provide context for our results.

10. Lines 292-295: is there a change in ozone sensitivity regime for any locations between the GEMS and TROPOMI products? Additionally, both TROPOMI and GEMS have ozone profile products, making it possible to assess variations in tropospheric ozone. Are these trends in the FNR and observed surface ozone from the air quality monitoring network consistent with the satellite-retrieved tropospheric ozone?

Response: We thank the reviewer for these insightful questions. We have added clarifications in the revised manuscript (Supplementary Fig. S6; lines 395–400). Below we address each question separately.

(1) Is there a change in ozone sensitivity regime between GEMS and TROPOMI?

We compared the ozone sensitivity partitioning from GEMS (using our LOESS-derived thresholds) and TROPOMI (using thresholds from Li et al., 2024, for consistency). As shown in Supplementary Fig. S6, the spatial distribution patterns of VOC-limited, transitional, and NO_x-limited regimes are highly consistent between the two datasets. Both identify the same major urban clusters with similar regime classifications. While minor differences exist in local numerical ranges (due to different overpass times and retrieval characteristics), the overall spatial structure is robust. This supports the reliability of our GEMS-based diagnostics.

(2) Are the FNR trends and surface O_3 consistent with satellite-retrieved tropospheric O_3 ?

We agree that this is an important consistency check. Although our study focuses on ozone formation sensitivity (via HCHO/NO_2) rather than tropospheric O_3 columns, we have examined this question using available literature and GEMS data. Specifically, previous validation studies have shown that GEMS tropospheric O_3 columns exhibit a

diurnal pattern consistent with surface O_3 observations (Kim, 2023), with ozone increasing through the morning and peaking in the afternoon (~15:00 LST). This diurnal phase matches the FNR-derived sensitivity trends (e.g., afternoon shifts toward transitional/NOx-limited regimes). Therefore, at large scales, the FNR-based sensitivity diagnosis is broadly consistent with both surface O_3 and satellite tropospheric O_3 variations. We have added this discussion in the revised manuscript (lines 287–290).

11. Lines 321-322: what do the two black lines represent on Figure 4a-h? How were they determined? Based on the caption, it appears this is based on the LOESS analysis, but I am confused how this would produce two values.

Response: We thank the reviewer for this question. The two black lines in Fig. 4a–h represent the boundaries of the ozone formation sensitivity transition zone, derived objectively from the LOESS analysis. As detailed in our response to the first specific comment and in the revised Methods section (lines 231–244), the LOESS fitting of the O_3–FNR relationship yields a peak (f_max), and the transitional regime is defined as the FNR interval where f(FNR) ≥ 0.9 × f_max. The endpoints of this interval are denoted as FNR_start (left black line) and FNR_end (right black line).
Thus:
FNR < left line → VOC-limited
FNR between the two lines → Transitional
FNR > right line → NO_x-limited
We have updated the Figure 4 caption to explicitly state this(lines 381–388).

12. Lines 380-382: what are these fractions of ozone formation regimes based on? Are the four cities being treated as a single point or several points within an area? How is this defined?

Response: We thank the reviewer for this clarifying question. We have added the following explanation to the revised manuscript (see lines 433–435) to define how the city-level fractions were calculated.
(1) What are these fractions based on?
They are based on spatial statistics within the administrative boundaries of each city, not on individual monitoring stations.
(2) Are the four cities treated as a single point or several points?
They are treated as areas (several points/pixels within the city boundary), not as single points.
(3) How is this defined?
Specifically, we obtained vector data of the administrative boundaries for the four cities, applied a spatial masking procedure to the hourly ozone formation sensitivity results (from Section 3.3, based on FNR thresholds), and calculated the area fractions of VOC-limited, transitional, and NO_x-limited regimes within each city. Percentages were then computed to derive the proportional characteristics for each city.

We have included this description in the revised manuscript to ensure transparency.

13. Lines 449-450: NO_x should also be mentioned here.
Response: We thank the reviewer. We have added NO_x to the sentence (lines 513–514) as suggested.

14. Line 452: was the data daily or hourly?
Response: We thank the reviewer. The data are hourly (09:00–16:00 LST). We have revised the text accordingly (lines 515–518).

15. Lines 505-506: when and how was land use remote sensing data used?
Response: We thank the reviewer for this careful observation. We would like to explain the history of this data and our handling of it in the current revision.
Background: In the original manuscript, land-use data were used to discuss urban–rural differences in ozone formation regimes. However, based on a first-round reviewer's suggestion to focus the paper on GEMS-based diurnal variations rather than urban–rural comparisons, we removed the urban–rural discussion in the initial revision. Unfortunately, we inadvertently retained the land-use data description in that revision. We appreciate the reviewer's keen eye in catching this.
Current revision: After reconsideration, we have decided to restore a little urban–rural analysis in a concise manner, as we believe it provides valuable context and may inspire future research on diurnal variations of ozone formation mechanisms across urban–rural gradients. Specifically, we have:
1)Added Supplementary Fig. S7 to visualize the spatial distribution of ozone formation regimes across urban and rural areas.
2)Integrated a brief discussion into Section 3.3 (lines 397–400), noting that VOC-limited regimes are more pronounced in urban centers, while suburban/rural areas are more often transitional or NO_x-limited.
Data processing (how): The land-use data are derived from the 2020 China Multi-period Land Use Remote Sensing Monitoring Dataset. The study area was classified into three categories: Urban, Rural, and Others. The processing steps were: (1) clipping to the study area and reprojecting to WGS84; (2) resampling to match GEMS grid resolution and reclassifying by pixel value (0=Others, 1=Urban, 2=Rural); (3) overlaying the classified raster with ozone regime maps for visualization (Fig. S7).
We thank the reviewer again for helping us correct this oversight and for supporting the inclusion of this scientifically relevant urban–rural perspective.

Suggested Technical Corrections

1. Lines 251-257: should the chemical mechanism be discussed in the results? This seems like something that should be discussed in the introduction along with the literature.

Response: We thank the reviewer for this structural suggestion. The content in lines 299–306 (original lines 251–257) is not a general introduction to photochemical mechanisms, but rather a physicochemical interpretation of our specific observational results (e.g., explaining why HCHO increases while NO_2 decreases diurnally). As such,

we believe it fits naturally in the Results and Discussion section to support the logical flow from observation to mechanism.
However, to address the reviewer's concern, we have added a brief overview of the relevant photochemical background in the Introduction (see lines 55–59) to provide readers with necessary context before reaching the Results section. We believe this compromise strengthens the manuscript without disrupting the result-specific interpretation.

2. Lines 277-279: this seems like an important result of the paper, but I did not understand exactly what was trying to be said here.

Response: We thank the reviewer for pointing out this lack of clarity. The intended message of the original sentence is that the afternoon photochemical environment shifts toward higher HCHO and lower NO_2, creating conditions conducive to O_3 production and leading to the daily O_3 peak. To make this clearer, we have revised the text in the manuscript (see lines 326–328) as follows:
"By the afternoon (Figs. 4e-h), the data points consistently cluster in regimes c haracterized by elevated HCHO and depleted NO_2, indicating a progressive shif t in the photochemical environment. Under these conditions, O_3 concentrations concurrently reach their diurnal maximum."

3. Lines 335-339: the discussion here was already presented on lines 279-283.

Response: We thank the reviewer for noting the redundancy. We have consolidated and streamlined the content in lines 395–422 (Original lines 335–339) into a single, non-redundant integrated discussion, covering spatial distribution characteristics, urban–rural differences, diurnal transitions, and regional-scale mechanisms (BTH, YRD, SC, PRD).

4. Lines 343-360: since there is a section specifically for comparing the four city clusters, should this part of the analysis be moved there?

Response: We thank the reviewer for the valuable suggestion. In the revised manuscript, Section 3.3 (regional patterns) and Section 3.4 (city-scale mechanisms) serve distinct purposes: the former focuses on spatial evolution across urban clusters, while the latter examines diurnal physicochemical drivers at the city level. Moving this analysis would blur this hierarchical structure.
To nonetheless improve cross-sectional coherence, we have added explicit cross-references between the two sections: at the end of Section 3.3 (lines 418–422) we now direct readers to Section 3.4 for city-scale analysis, and at the opening of Section 3.4 (lines 432–435) we link back to the regional patterns discussed in Section 3.3.
We believe these revisions address the reviewer's concern while preserving the intended logical flow. We again thank the reviewer for the insightful comment.

5. Line 380: typo ("environmen" instead of environment).

Response: We thank the reviewer for catching this typo. It has been corrected to "environment" (see line 444).

6. Lines 428-429: this sentence does not make sense.

Response: We thank the reviewer for pointing this out. The original sentence was indeed trivial. We have rephrased it to link the meteorological conditions to ozone formation regimes (see lines 491–493):

"Among the four cities, Guangzhou exhibits the highest T_{2m} and RH, which may enhance photochemical reaction rates and contribute to the observed shift toward NO_x-limited regimes in the afternoon."

7. Line 460: type ("levles" instead of levels).

Response: We thank the reviewer for catching this typo. It has been corrected to "levels" (see line 524).

8. Line 470: ranges of numbers do not require brackets in the text.

Response: We thank the reviewer for the suggestion. The brackets have been removed (see lines 532–533).

Reviewer #2:

In response to the comments raised by Reviewer #2, we will address them in three parts below.

(1) This paper adds an important new data set to the discussion of ozone production and concentrations in rural and urban China. The observations and the description of diurnal variation are worthy of publication as a data set. However the aspects of those paper that interpret those observations are severely lacking and I cannot recommend publication.

Response: We sincerely thank the reviewer for recognizing the value of the GEMS dataset and the diurnal observations as "worthy of publication as a data set." We agree that the unique value of this dataset lies precisely in its ability to reveal the diurnal evolution of ozone formation sensitivity, providing new insights into how ozone formation mechanisms may change dynamically during the daytime.

We take seriously the reviewer's concern that the interpretive aspects were lacking in the original manuscript. To address this, we have substantially revised the manuscript with a number of improvements across multiple sections, for example:

1)Quantitative analysis of pollutant–meteorology relationships (Section 3.1)

2)GEMS vs. TROPOMI cross-sensor validation (Section 3.2)

3)Spatial validation of ozone formation regimes (Supplementary Fig. S6)

4)LOESS-based sensitivity classification with bootstrap uncertainty (Section 3.2; Section 3.3)

5)Discussion of aerosol–HO_2 heterogeneous chemistry as an additional regulatory mechanism (Conclusions and Outlook)

Below we elaborate on several of these enhancements:

1) Enhanced physicochemical interpretation of diurnal pollutant variations (Section 3.1, lines 255–276; Table S1; Figs. S1–S4)

We have added a dedicated mechanistic discussion explaining why HCHO increases and NO_2 decreases diurnally. Specifically, we added hourly spatial distribution maps of T_{2m}, RH, SSR, and BLH, and performed Spearman correlation analysis. The results show that HCHO is significantly positively correlated with T_{2m} ($\rho = 0.531$, $p < 0.01$) and SSR ($\rho = 0.415$, $p < 0.01$), while NO_2 is significantly negatively correlated with T_{2m} ($\rho = -0.556$, $p < 0.01$) and BLH ($\rho = -0.201$, $p < 0.01$). These findings quantitatively support the photochemical drivers of diurnal variations. We also explicitly link these trends to photochemical reaction equations (Eqs. 1–4) and cite relevant observational studies.

2) Quantitative cross-sensor validation (GEMS vs. TROPOMI) (Section 3.2, lines 344–356; Supplementary Fig. S5)

To address potential concerns about data reliability, we conducted a systematic comparison between GEMS and TROPOMI HCHO, NO_2, and FNR products. The analysis includes Pearson correlation ($r = 0.838$ for NO_2, 0.506 for HCHO, and 0.783 for FNR) and mean bias. The strong agreement for FNR ($r = 0.783$) confirms that GEMS-derived ozone sensitivity is robust.

3) Spatial validation of ozone formation regimes (Supplementary Fig. S6)

We added spatial distribution maps of ozone formation regimes derived from both GEMS and TROPOMI data. The results show high consistency between the two datasets in the spatial distribution of VOC-limited, transitional, and NO_x-limited regimes, further supporting the reliability of our GEMS-based diagnostics.

4) LOESS-based sensitivity classification with bootstrap uncertainty (Section 3.2, lines 357–379; Section 3.3, lines 395–422)

To provide a rigorous and objective definition of ozone sensitivity regimes, we applied LOESS regression to the O_3–FNR relationship and used bootstrap resampling (1000 iterations) to estimate the 95% confidence interval of the fitted curve. This allows us to quantitatively define VOC-limited, transitional, and NO_x-limited regimes based on the endpoints (FNR_start, FNR_end) of the high-response interval ($f(FNR) \geq 0.9 \times f_{max}$).

5) Acknowledgment of additional regulatory mechanisms (Conclusions and Outlook, lines 559–570)

In response to the reviewer's suggestion, we now explicitly acknowledge in the Conclusions that aerosol effects (e.g., heterogeneous HO_2 uptake) represent a "third dimension" regulating O_3-NO_x-VOC sensitivity beyond the traditional NO_x-VOC framework. We identify this as a key limitation of the current study and an important direction for future research.

We believe these revisions have fundamentally strengthened the interpretive depth of the manuscript, moving it beyond a mere data description to a process-oriented analysis. We thank the reviewer for pushing us to improve the work.

(2) Interpretation of surface observations of ozone, VOC and nitrogen oxides have driven a wealth of publications and creative thinking about ozone in Chinese cities and in rural Chinese locations. This paper does little to characterize the state-of-the-art in our communities thinking about ozone production and as such it is almost impossible to understand if the new satellite remote sensing data confirms current understanding or contradicts it.

Response: We sincerely thank the reviewer for this critical comment. We agree that a clear connection to the existing literature is essential for readers to understand whether our GEMS-based results confirm or challenge current understanding of ozone formation mechanisms. The reviewer raises two distinct but related questions: (1) how our results relate to existing findings (confirm or challenge/extend), and (2) whether we have adequately surveyed and connected our work to cutting-edge mechanistic understanding (e.g., VOC reactivity, radical cycling, HO_2 heterogeneous uptake). Below we address both.

Question 1: Does our study confirm or challenge existing understanding?

We have systematically compared our GEMS-based results with the existing literature. The answer is: mostly confirm, but significantly extend.

What our results confirm:

1)HCHO increases with temperature and solar radiation, consistent with VOC photochemical oxidation (Wu et al., 2023);

2)NO_2 decreases due to photochemical loss and boundary layer dilution, consistent with known NO_2 photochemistry (Xie et al., 2016);

3)The FNR-based spatial patterns (e.g., NO_x-limited in most regions, VOC-limited in urban centers) align with previous studies (Li et al., 2024; see also the Supplement).

What our results extend (new insights that previous daily-scale studies could not resolve):

1)Ozone formation sensitivity is not static but changes systematically from morning to afternoon;

2)Many urban areas transition from VOC-limited in the morning to transitional or NO_x-limited in the afternoon;

3)This diurnal dynamic varies by region (e.g., PRD shifts to NO_x-limited, while SC remains VOC-limited).

Conclusion: Our findings do not contradict existing theory. Rather, they add a critical temporal dimension that refines our understanding of when and how ozone formation regimes shift during the day.

Question 2: How have we connected our work to cutting-edge mechanistic understanding?

We agree that the Introduction should survey the state-of-the-art, and the Discussion should indicate how our results relate to these advanced mechanisms (even if not directly tested). Accordingly, we have made the following revisions to the manuscript:

1) Expanded Introduction on cutting-edge mechanisms (lines 40–55)

We have added three paragraphs covering:

(a) VOC composition and reactivity:

Alkenes, aromatics, and OVOCs play key roles in radical generation and propagation. Carbonyl compounds contribute up to 48.3% of OFP, and HCHO photolysis provides ~70.1% of HO_2 source (Yao et al., 2025).

(b) Radical cycling processes:

$OH–HO_2–RO_2$ cycling coupled with NO_x directly determines ozone production efficiency. Daytime peak HO_2/RO_2 concentrations reach $10^8–10^9$ molecules cm^{-3} and correlate well with O_x production rates (Bottorff et al., 2023).

(c) Source-dependent VOC reactivity:

Anthropogenic vs. biogenic VOCs differ substantially in their contributions to ozone formation, reinforcing the view that reactivity governs ozone production (Ye et al., 2026; Qin et al., 2025;Li et al., 2026).

In addition, to ensure that the fundamental photochemical processes underlying our confirmatory findings are properly cited, we have added the following sentence to the Introduction (lines 55–59):

"Beyond these complex mechanisms, the fundamental photochemical processes controlling diurnal variations are relatively well understood: HCHO concentrations increase with temperature and solar radiation, primarily due to VOC photochemical oxidation (Wu et al., 2023), whereas NO_2 concentrations decrease as a result of photochemical loss and boundary layer dilution (Xie et al., 2016)."

2) Revised the Conclusions and Outlook section to address the "confirm versus extend" question and to clarify the consideration of advanced mechanisms.

We have added a comprehensive statement in the Conclusions and Outlook section to directly address the "confirm versus challenge" question, while objectively acknowledging the limitations of the satellite-based approach in resolving complex mechanisms (lines 552–570)

"In summary, our GEMS-based results largely confirm the existing mechanistic understanding: HCHO increases with enhanced photochemical activity, NO_2 decreases due to photochemical loss, and the FNR-based spatial patterns are consistent with previous studies. Building upon this foundation, our study further provides an important extension by revealing, for the first time, the diurnal dynamics of ozone formation sensitivity—specifically, that many urban areas transition from VOC-limited conditions in the morning to transitional or NO_x-limited regimes in the afternoon. Therefore, our findings do not contradict existing theory; rather, they introduce a critical temporal dimension that cannot be resolved by previous satellite studies limited to daily-scale observations. Nevertheless, we acknowledge that several advanced mechanistic aspects are not directly addressed in this study. These include the specific roles of different VOC species (e.g., carbonyls versus aromatics) in radical production, the coupled effects of heterogeneous HO_2 uptake and aerosol radiative processes on radical cycling and $O_3–NO_x–VOCs$ sensitivity (i.e., the so-called "third dimension") (Dyson et al., 2023; Wang et al., 2022; Li et al., 2018), as well as the differential contributions of anthropogenic and biogenic VOCs to ozone formation. Future research

will further advance within a multi-process coupled framework by integrating regional air quality models, high-resolution anthropogenic VOC emission inventories, and aerosol–radiation interactions, while explicitly incorporating key mechanisms such as heterogeneous HO_2 loss, to systematically elucidate the nonlinear response characteristics of O_3–VOCs–NO_x, thereby providing more robust scientific support for precise emission reduction and coordinated control strategies across different periods and regions."

3) Acknowledged HO_2 heterogeneous uptake as a "third dimension" (Conclusions and Outlook, lines 560–564)
As detailed in our response to Question 3, we have added a dedicated discussion in the Conclusions explicitly acknowledging that aerosol effects (e.g., HO_2 uptake) represent a third dimension regulating O_3–NO_x–VOC sensitivity, citing the recommended literature (Dyson et al., 2023; Wang et al., 2022; Li et al., 2018).

4) Revised statement of study objective (lines 148–152)
To avoid any misunderstanding about the purpose of our study, we have rephrased the research objective as follows:
"It should be noted that the primary objective of this study is not merely to validate existing understanding, but rather to extend it by leveraging the hourly temporal resolution and broad spatial coverage of GEMS observations to reveal the diurnal dynamics of ozone formation sensitivity—an aspect that previous satellite-based studies, largely constrained by once-daily overpasses, have been unable to resolve."

We thank the reviewer for pushing us to better position our work within the existing literature and to connect it to cutting-edge mechanistic understanding. We believe the revised manuscript now makes the relationship between our findings and current knowledge clear and transparent.

(3) I note an active literature on the role of heterogeneous uptake of HO_2 and thus a third dimension of aerosol control in addition to NO_x and VOC control. I also note that it is important to be clear about whether the paper is interested in instantaneous ozone and ozone production or net production leading to high values in the afternoon. A small sampling of references are listed below. I do not attempt a comprehensive list. Other important references will be found in these papers and elsewhere.

T. Chen, B. Chu, J. Ma et al., Ozone Pollution in China: Current Status and Control Strategies, Engineering, https://doi.org/10.1016/ j.eng.2025.06.044

Dyson, J. E., Whalley, L. K., Slater, E. J., Woodward-Massey, R., Ye, C., Lee, J. D., Squires, F., Hopkins, J. R., Dunmore, R. E., Shaw, M., Hamilton, J. F., Lewis, A. C., Worrall, S. D., Bacak, A., Mehra, A., Bannan, T. J., Coe, H., Percival, C. J., Ouyang, B., Hewitt, C. N., Jones, R. L., Crilley, L. R., Kramer, L. J., Acton, W. J. F., Bloss, W. J., Saksakulkrai, S., Xu, J., Shi, Z., Harrison, R. M., Kotthaus, S., Grimmond, S., Sun,

Y., Xu, W., Yue, S., Wei, L., Fu, P., Wang, X., Arnold, S. R., and Heard, D. E.: Impact of HO2 aerosol uptake on radical levels and O_3 production during summertime in Beijing, Atmos. Chem. Phys., 23, 5679–5697, https://doi.org/10.5194/acp-23-5679-2023, 2023.

Li, C., Zhu, Q., Jin, X., and Cohen, R.C.: Elucidating Contributions of Anthropogenic Volatile Organic Compounds and Particulate Matter to Ozone Trends over China, Environ. Sci. Technol. 2022, 56, 18, 12906–12916.

Jie Li, Xueshun Chen, Zifa Wang, Huiyun Du, Weiyi Yang, Yele Sun, Bo Hu, Jianjun Li, Wei Wang, Tao Wang, Pingqing Fu, Huili Huang, Radiative and heterogeneous chemical effects of aerosols on ozone and inorganic aerosols over East Asia, Science of the Total Environment 622–623 (2018) 1327–1342 doi.org/10.1016/j.scitotenv.2017.12.041

Ye, X., Zhang, L., Wang, X., Lu, N., Hickman, S., Luo, G., and Archibald, A. T.: Deciphering the impacts of meteorology on surface ozone variability in eastern China using explainable machine learning models, EGUsphere [preprint], https://doi.org/10.5194/egusphere-2026-74, 2026.

Response: We sincerely thank the reviewer for providing these important references and for raising two critical conceptual issues: (1) the role of heterogeneous HO_2 uptake as a "third dimension" of aerosol control, and (2) the need to clarify whether we address instantaneous sensitivity or net production. We have addressed both concerns as detailed below.

We have carefully reviewed all the papers recommended by the reviewer, as well as several additional relevant studies identified from their reference lists. Key insights from these papers have been incorporated into the revised manuscript as follows:

Chen et al. (2025) → cited in the Introduction (lines 38–39) to support the increasing trend of ozone in China, thereby motivating the discussion of recent advances in ozone formation mechanisms.

Dyson et al. (2023) and Li et al. (2018) → cited in the Conclusions and Outlook (lines 560–564) as direct observational evidence of heterogeneous HO_2 uptake on aerosol surfaces affecting radical levels and ozone formation.

Li et al. (2022) → cited in the Introduction (lines 45–48) to support the role of radical cycling processes and their coupling with NO_x in regulating ozone formation.

Ye et al. (2026) → cited in the Introduction (lines 50–55) to illustrate the influence of meteorological conditions on ozone variability.

Additional references retrieved from the recommended papers:

Li et al. (2025) → cited in the Introduction (lines 40–42) to support the contribution of VOCs to ozone formation.
Qin et al. (2025) → cited in the Introduction (lines 50–55) to indicate that high temperature and heatwave events enhance ozone formation by accelerating photochemical reaction rates, reinforcing the concept that reactivity, rather than concentration alone, governs ozone production.
Wang et al. (2022) → cited in the Conclusions (lines 560–564) to support the impact of heterogeneous HO_2 loss on ozone formation over the North China Plain. This study serves as one of the key pieces of evidence for the role of heterogeneous HO_2 uptake as a "third dimension", complementing Dyson et al. (2023) and Li et al. (2018).
Zhang et al. (2026b) → cited in the Introduction (lines 45–48) to support the discussion of seasonal atmospheric oxidizing capacity (AOC) and radical chemistry over North China. This study is used to substantiate the role of OVOCs in radical cycling discussed in the Introduction and is consistent with the findings of Bottorff et al. (2023).
Li et al. (2026) → cited in the Introduction (lines 50–55) to illustrate the contribution of primary OVOCs to HO_2 production and ozone formation. This study supports the discussion of VOC reactivity in the Introduction and is consistent with the regional analyses of the Pearl River Delta (PRD) and Sichuan Basin (SC) presented in the Results section.

We thank the reviewer for pointing us to this important body of work.

1) Aerosol effects and heterogeneous HO_2 uptake (the"third dimension")
We agree with the reviewer that aerosol-related processes (e.g., HO_2 heterogeneous uptake, aerosol radiative effects) represent an important regulatory mechanism beyond the traditional NO_x-VOC framework. In the revised manuscript, we have added a dedicated discussion in the Conclusions and Outlook section (lines 559–570) that explicitly:
(a) Acknowledges that our current analysis does not account for these processes;
(b) Cites the recommended literature (Dyson et al., 2023; Li et al., 2018) to support the importance of this "third dimension";
(c) Identifies this as a key limitation of the present study;
(d) Outlines future directions to incorporate aerosol–radiation–photochemistry interactions and heterogeneous HO_2 loss into a multi-process coupled framework.

2) Clarification: instantaneous ozone formation sensitivity vs. net production
The reviewer raises an important distinction. We have clarified in the revised manuscript (Introduction, lines 153–157) that this study focuses on the sensitivity of ozone formation under instantaneous photochemical conditions (i.e., the regime classification: VOC-limited, transitional, NO_x-limited) rather than on the quantitative decomposition of net ozone production ($P(O_3)$–$L(O_3)$) that leads to afternoon peak concentrations.

Specifically:
What we do: Diagnose ozone formation sensitivity using the $HCHO/NO_2$ ratio (FNR) from hourly GEMS observations. This indicates whether ozone production is more sensitive to NO_x or VOCs under given photochemical conditions.
What we do not do: Quantitatively calculate net ozone production rates or separate the cumulative effects of emissions, photochemistry, and boundary layer development that produce the afternoon O_3 maximum.
We have added the following text to the Introduction (lines 146–157) to make this distinction clear:
"Based on this, we systematically investigate the hourly spatiotemporal evolution of FNR over China during the warm seasons of 2021–2023 (09:00–16:00 LST), thereby elucidating the intraday transitions in ozone formation regimes and their key driving factors. It should be noted that the primary objective of this study is not merely to validate existing understanding, but rather to extend it by leveraging the hourly temporal resolution and broad spatial coverage of GEMS observations to reveal the diurnal dynamics of ozone formation sensitivity—an aspect that previous satellite-based studies, largely constrained by once-daily overpasses, have been unable to resolve. Meanwhile, the formation of high ozone concentrations in the afternoon is typically the result of the cumulative effects of multiple processes, including emissions, photochemical reactions, and boundary layer development. This study does not explicitly separate or quantitatively decompose these cumulative processes; instead, it provides observational constraints from the perspective of instantaneous formation sensitivity."

Summary:
We thank the reviewer again for these insightful comments. The revised manuscript now:
(a) Explicitly acknowledges aerosol–HO_2 heterogeneous chemistry as a "third dimension"and a key limitation (Conclusions and Outlook);
(b) Clearly distinguishes between instantaneous sensitivity diagnosis and net production quantification (Introduction);
(c) Cites all the recommended references in appropriate sections.