

Point-to-point responses

*We appreciate the reviewers for their valuable and constructive comments, which are very helpful for the improvement of the manuscript. We have revised the manuscript carefully according to the reviewers' comments. We have addressed the reviewers' comments on a point-to-point basis as below for consideration, where the reviewers' comments are cited in **black**, and the responses are in **blue**.*

Referee #1

This study presents a valuable dataset comprising vertical profiles of HONO and O₃ obtained from the Chinese Hyperspectral Vertical Remote Sensing Network between 2021 and 2024. The work addresses a critical gap in vertical observations of key photochemical species over China, offering substantial scientific insight into tropospheric atmospheric oxidative capacity and photochemical pollution mechanisms. The dataset spans 22 representative sites with extensive spatial and temporal coverage, and has been processed using a consistent and rigorous methodology, including the use of the TUV model to calculate photolysis frequencies and OH production rates. The manuscript is well-structured, effectively supported by figures, and the independent validation results are compelling. The dataset holds high practical value for improving chemical transport models and informing air quality policy, and thus meets the journal's publication standards. However, several issues pertaining to the clarity of methodological descriptions and internal consistency of the data require the authors' attention, as detailed below.

1. Line 61: Could the authors clarify whether the dataset used in this study includes stations located in these regions?

Re: Thank you for your comments. The reference to “these regions” in the original manuscript was indeed unclear, leading to ambiguity. We hereby clarify that the dataset constructed in this study (i.e., the 2021–2024 Chinese Hyperspectral Vertical Remote Sensing Network dataset) does include stations in the five major regions mentioned earlier: North, East, South, Southwest, and Central China. Specifically, the dataset consists of observational data from 22 stations distributed across these five major regions (see Table 1 for details). The original phrasing was intended to introduce the spatial coverage of the dataset, but it was poorly worded. We have revised the relevant sentence in the manuscript to: “In contrast, ozone (O₃)—a secondary pollutant and a major atmospheric oxidant—has continued to increase, particularly in economically developed regions such as the Beijing–Tianjin–Hebei area, the Yangtze River Delta, and the Pearl River Delta. To address the observational gaps in these and other key regions, we developed a comprehensive dataset. The dataset comprises measurements from 22 ground-based sites across five major regions of China—North, East, South, Central, and Southwest China.” Through this revision, we explicitly link the

dataset to these key regions, eliminating any ambiguity.

2. Line 138: The authors should clarify the criteria used for selecting the monitoring sites (e.g., representativeness, pollution level, climate zone, or instrument deployment feasibility) to better justify the spatial representativeness of the dataset.

Re: Thank you for your comments. Site selection is the foundation for building a scientifically meaningful network. We described the representativeness of each site in Section 2.1, but we did not summarize them into explicit “selection criteria.” Now, we supplement and explicitly articulate that the network site selection followed the following multi-dimensional criteria, which collectively ensure the spatial representativeness of the dataset: (1) Representativeness of atmospheric environments: The aim was to cover major topographical and underlying surface types in China (plains, basins, mountains, plateaus, coasts), climate zones (temperate, subtropical), and typical pollution versus clean background conditions. For example, urban sites in the North China Plain, basin sites in Sichuan, high-altitude sites on the Tibetan Plateau/Mount Tai, and coastal sites in the Pearl River Delta. (2) Diversity of pollution levels and types: Sites were selected to encompass a gradient ranging from heavily polluted urban areas, urban-suburban transition zones, and regional background areas to clean background areas minimally affected by human activities (e.g., the Mount Tai TS site). (3) Orientation towards key scientific questions: The selection of some sites directly served specific scientific objectives. For example, the North China site cluster was used to study photochemical processes in the heavily polluted Beijing-Tianjin-Hebei region; the dense cluster in the Pearl River Delta (e.g., GZ_ZL, GZ_NS) was used to resolve fine-scale transport and mixing within cities; Southwest basin sites (CQ, CDAES) were used to investigate pollution accumulation mechanisms under stagnant weather and high humidity; mountain sites (SXU, TS) were used to assess topographical impacts and stratosphere-troposphere exchange. (4) Feasibility of actual deployment: Sites had to meet the technical requirements for ground-based MAX-DOAS observations, such as having an unobstructed field of view (especially at low elevation angles), stable power supply, a secure observation environment, and being affiliated with research institutes or universities to ensure long-term, stable operation and maintenance.

3. Lines 156-160: The Mount Tai (TS) site is defined as a clean background station. However, as a tourist attraction surrounded by industrial provinces, is there any interference in the observational data caused by tourism traffic or transport from surrounding industries? It is recommended to discuss the reliability of its background attributes.

Re: Thank you for your comments. The representativeness of the Mount Tai site as a high-altitude clean background site indeed requires more rigorous argumentation. First, the observational data themselves

support its clean background attributes: as shown in Figure 3, the HONO concentration at the Mount Tai site remained below 0.1 ppb throughout the day, much lower than urban sites in the same region (e.g., 0.2–0.3 ppb at NUIST and AHU), indicating minimal impact from direct near-surface emissions. O₃ also exhibited typical clean background vertical distribution characteristics (low at lower levels, high aloft, gentle diurnal variation) without significant anthropogenic photochemical enhancement signals. However, potential interferences cannot be ignored: (1) Tourism traffic: As a famous scenic spot, tourist and vehicle activities may generate local NO_x and VOCs emissions at the foot and mid-section of the mountain. However, these emissions are mainly concentrated in the lower and middle-lower parts of the mountain body. The TS site is located at the summit at an altitude of 1500 m; the path atmosphere it observes mainly comes from the lower free troposphere and higher air masses, with a low probability of direct pollution from local emissions at the lower part of the mountain, and it is more likely to be influenced by regional or long-range transport. (2) Regional industrial transport: There are indeed industrial provinces (e.g., Shandong, Hebei) surrounding Mount Tai. However, when industrial pollution plumes are transported to the summit, it usually results in obvious pollution episodes, manifesting as an overall increase in O₃, aerosols, and other concentrations. The dataset we present is the “mean” vertical profile from 2021 to 2024; such sporadic transport events are smoothed out in the long-term average and do not become a dominant feature. Therefore, we believe that for studying the climatological average background photochemistry of the free troposphere, assessing stratospheric contributions, and serving as a reference point for pollution transport, the Mount Tai site still has reliable representativeness.

4. Lines 185-187: The manuscript mentions the use of a standardized instrument configuration. Please supplement the specific brand and model of the spectrometers used at different sites (e.g., whether they are all the same model), which is crucial for assessing instrument consistency and data comparability.

Re: Thank you for your comments. Instrument consistency is the foundation for ensuring the comparability of multi-site data. The “standardized instrument configuration” stated in the text indeed requires more specific explanation. The spectrometers used at all 22 sites in this network are of the exact same model. Before being shipped to each site, these instruments all underwent unified wavelength calibration, stray light testing, and radiometric calibration in the laboratory, ensuring consistency in instrument performance. The telescope parts (including prisms and lenses) were also processed following unified design specifications. Therefore, it can be confirmed that the instrument hardware used in this dataset is completely consistent in terms of brand, model, and initial performance, which provides a solid hardware foundation for the internal consistency of the data. The only difference is that the instruments at different sites were set up at different times and have operated for different durations, but the instrument specifications are identical.

5. Lines 188-190: Regarding the telescope design, please confirm whether “field of view <math><0.3^\circ</math>” refers to the full field of view or the half field of view.

Re: Thank you for your comments. We explicitly clarify here that the “field of view <math><0.3^\circ</math>” stated in the text refers to the full field of view. In MAX-DOAS observations, a smaller field of view is crucial for improving spatial resolution and reducing side-scattering interference from the lower atmosphere. A full field of view of

6. Lines 190-191: The manuscript mentions that the spectrometer covers ultraviolet (296–408 nm) and visible (420–565 nm) ranges, with a gap of approximately 12 nm between them. Does this spectral gap affect the retrieval of specific species?

Re: Thank you for your comments. This is a very professional technical question. In short, this spectral gap of approximately 12 nm (408–420 nm) does not affect the retrieval of the core target species (HONO, O₃, O₄) in this dataset. The reason is that in DOAS spectral fitting, we used specific, narrow fitting windows for different species (see Table 2 for details), and these fitting windows all fall entirely within the effective coverage of the spectrometer, avoiding the gap region: (1) HONO: The retrieval band is in the 335–373 nm range (see Table 2), completely within the ultraviolet band. (2) O₃: Retrieval primarily uses 320–340 nm (see Table 2), also within the ultraviolet band. (3) O₄: As a key for aerosol retrieval, it mainly uses the ultraviolet channel of 338–370 nm and the visible light channel near 477 nm. The visible channel (420–565 nm) covers the area near 477 nm, so the O₄ retrieval in visible light is not affected. However, the retrieval in this study uses 338–370 nm, so there is no impact whatsoever. Although the gap (408–420 nm) band may contain some weak absorption information, it is not located at the center of the strong absorption bands of our main species of interest (HONO, O₃). Furthermore, DOAS retrieval relies on the overall fitting of differential absorption structures within the selected fitting window, rather than dependence on continuous coverage of the entire spectrum. Therefore, this gap does not have a substantial impact on the retrieval accuracy of the HONO and O₃ vertical profiles in this study.

7. Lines 193-194: All sites employed an identical elevation scanning sequence, yielding a full scan cycle of ~12 min. Does this scan cycle refer to the total time to complete all elevation measurements (from 1° to 90°) and be ready to start the next round of scanning?

Re: Thank you for your comments. The reviewer’s understanding is completely correct. The “full scan cycle of ~12 min” in our text refers to the total time required to complete a full elevation scanning sequence (all observation angles from 1° to 90°) and be ready to start the next round of scanning. Specifically, the

integration time for each elevation angle is 1 minute, and the total integration time for 11 observation angles (1°, 2°, 3°, 4°, 5°, 6°, 8°, 10°, 15°, 30°, 90°) is 11 minutes. The remaining approximately 1 minute is used for the stepper motor to drive the telescope to move to the next angle and stabilize. Therefore, from the start of the observation at the first 1° angle to the start of the next cycle's first 1° angle, approximately 12 minutes elapse. This temporal resolution is sufficient to capture boundary layer photochemical processes on the scale of minutes to hours. We have revised “yielding a full scan cycle of ~12 min” to “yielding a full scan cycle of approximately 12 min, which is the total time to complete all elevation measurements and be ready to initiate the next scanning cycle” in the revised manuscript to make the expression clearer and unambiguous.

8. Line 199: “To minimize stratospheric contamination, spectra acquired at solar zenith angles greater than 75° were excluded.” Is this filtering criterion applied only to daytime measurement data, or does it also apply to nighttime measurements?

Re: Thank you for your comments. This filtering criterion is applied only to daytime observation data. The reason is as follows: we stated in Section 2.2, “Routine measurements were conducted during daytime (08:00–18:00 local time). The instruments also operated at night to record dark current and electronic offsets...”. Therefore, the raw spectral data acquired at night were not intended for retrieving vertical profiles of various species in the first place; their purpose was to perform instrument dark current and offset calibration, and these calibration values were subsequently applied in the daytime spectral retrieval process. Only daytime spectra (08:00–18:00) enter the subsequent DOAS retrieval and profile inversion workflow. The filtering of solar zenith angle (SZA) > 75° is to avoid severe contamination of the lower atmosphere by stratospheric O₃ absorption during the sunrise and sunset transition periods, which is obviously a condition set for daytime photochemical research. Therefore, this criterion is not applied to nighttime data because nighttime data do not participate in chemical species retrieval. We have revised the sentence in the revised manuscript to: “To minimize stratospheric contamination, daytime spectra acquired at solar zenith angles greater than 75° were excluded from further analysis.” thereby clarifying its scope of application.

9. Lines 203-205: Please specify the exact version number of the QDOAS software, as different versions may contain different algorithm optimizations.

Re: Thank you for your comments. Thank you to the reviewer for the reminder. The precision of the software version number is crucial for the reproducibility of the study. The version of the QDOAS software we used in the retrieval is QDOAS 3.2. We have added this information in Section 2.3 of the revised manuscript: “Ultraviolet–visible spectra measured by the ground-based instruments were analysed with the QDOAS software (version 3.2) developed by BIRA-IASB.”

10. Lines 205-208: In the spectral retrieval section, it is explained that the zenith spectrum was used as the reference and subtracted from spectra at lower elevation angles. Is the zenith reference spectrum the 90° spectrum from the same scanning sequence, or an averaged or a specific time-interval zenith spectrum of the day?

Re: Thank you for your comments. The zenith reference spectrum we use is the 90° elevation spectrum from the same scanning sequence as the low-elevation spectrum to be retrieved. This is a standard practice in MAX-DOAS retrieval, known as the “Sequential Reference method.” Its advantage lies in: being able to maximally cancel out changes in solar radiation intensity, instrument response drift, and slow-varying absorption contributions from the upper atmosphere (stratosphere and above) within a short period (approximately a 12-minute scanning cycle). If the time interval between the zenith spectrum and the low-elevation spectrum within the same sequence does not exceed a few minutes, these “slow-changing” factors can be considered identical, and thus are effectively eliminated during the differencing process, highlighting the differential absorption signals brought by the lower atmosphere. We do not use an averaged zenith spectrum for the day or a zenith spectrum from a specific time interval, as that would introduce uncertainties due to changes in solar zenith angle and optical path differences. We have clarified this in the revised manuscript: “For each elevation scan, the zenith spectrum (90° elevation) acquired within the same scanning sequence was used as the reference...”

11. Line 207: Using the zenith spectrum as a reference spectrum is a standard DOAS practice. Is the integration time for the zenith spectrum the same as for low-elevation spectra? If not, how are differences in signal-to-noise ratio handled?

Re: Thank you for your comments. In our observation scheme, the zenith spectrum (90°) and all low-elevation spectra use the exact same integration time, which is 1 minute. This design was intentional, aiming to simplify the data processing workflow and maintain consistency. Using the same integration time means: (1) Differences in signal-to-noise ratio (SNR) naturally exist: the optical path for low-elevation spectra is longer, and under clear sky conditions, the radiation intensity they receive (especially scattered light) is usually higher than or close to the zenith direct light (depending on solar angle and aerosol conditions). Therefore, the SNR of low-elevation spectra may be slightly higher or similar to that of the zenith spectrum, and generally, the SNR of the zenith spectrum will not be significantly better than that of low-elevation spectra. (2) Robustness of DOAS fitting: DOAS retrieval is based on linear fitting of differential optical absorption. Modern DOAS algorithms (such as QDOAS) automatically assign weights based on the noise characteristics of each spectrum (which can be assessed via fitting residuals) during the fitting process and output fitting errors. The subsequent profile retrieval (OEM) also explicitly uses the

measurement error covariance matrix as input, which can be constructed based on DOAS fitting errors. Therefore, even if there are subtle differences in SNR among spectra at different elevation angles, this information is explicitly propagated into the subsequent retrieval uncertainty assessment, thereby being properly handled in the final results.

12. Lines 262-264: Figure 2 summarizes the monthly data completeness. It is suggested that the authors analyze whether the main reasons for missing data at different sites show seasonal differences (e.g., heating season in North China or rainy season in South China) and briefly explain this in the manuscript.

Re: Thank you for your comments. This is an excellent suggestion that can enhance the understanding of the operational background of the dataset. We have analyzed the reasons for missing data at each site and indeed found obvious seasonal differences, briefly explained as follows: (1) North China region (e.g., CAMS, SJZ_LC, etc.): During the winter heating season (November to March of the following year), the data missing rate may increase slightly. Reasons include: extreme low temperatures and icy/snowy weather may affect the stability of instrument operation; occasional instability in energy supply; and severe haze weather leading to extremely high atmospheric optical thickness, exceeding the effective range of the retrieval algorithm (insufficient DOF or large fitting errors). (2) South China/Southwest China regions (e.g., Guangzhou site cluster, CQ, CDAES, etc.): During the rainy season (April to September in South China, May to October in Southwest China), the main reasons for missing data shift to weather-related causes such as continuous precipitation, severe convective weather, and thick cloud cover. These weather conditions not only directly block observations but also cause aerosol wet growth, worsening retrieval conditions. (3) Missing data caused by occasional hardware failures are distributed throughout all seasons of the year without obvious seasonal preference.

13. Lines 268-270: It is mentioned that “more than ~85% of the sites operated for over one year, and ~60% for more than two years”. Does “operated” refer to completely continuous operation, or does it allow for interruptions while the data chain remains valid?

Re: Thank you for your comments. The meaning of “operated” here allows for interruptions, provided that the interruptions do not destroy the validity and continuity of the data. Specifically, “operated for over one year” means that from its start date to its stop or data cutoff date, the total time span of the site exceeds one year. Within this time span, there may be data gaps at the daily, weekly, or even monthly levels due to the aforementioned reasons (weather, maintenance, failures). As long as these gaps are explicitly marked as invalid in the dataset, and the remaining valid data sequence can constitute a “fragmented but valid” time chain that supports statistical analysis of seasonal and diurnal characteristics, we consider the site to be

“operated.” Our dataset quality control workflow (Section 2.4) ensures that all profiles entering the final dataset pass strict standards. Therefore, “operated” emphasizes that the site possesses the capability and experience to obtain valid data over the long term, rather than guaranteeing data at every moment of every day. We have revised the sentence in the revised manuscript to: “More than 85% of the sites had operational histories spanning over one year, and 60% for more than two years, although these periods may include intermittent data gaps due to maintenance, weather, or technical issues, with only quality-controlled valid profiles retained in the dataset.”

14. Lines 502-512: The peak $J(\text{HONO})$ at North China sites is approximately $2.5 \times 10^{-3} \text{ s}^{-1}$. How does this value compare with other similar studies (e.g., field measurements in urban Beijing)? Please add comparative discussion.

Re: Thank you for your comments. We compared it with some previous studies: (1) Comparison with urban observations in Beijing: Our peak values ($0.0020\text{--}0.0025 \text{ s}^{-1}$) are highly consistent with the midday peak $J(\text{HONO})$ ($\sim 0.0022 \text{ s}^{-1}$) observed using MAX-DOAS in the suburbs of Beijing by He et al.(2023). This verifies the reliability of our dataset in the Beijing region. (2) Comparison with other domestic and international sites: Our values are also within the typical range of midday peak $J(\text{HONO})$ reported internationally for urban/suburban areas. For example, peaks observed in Madrid, Spain, were approximately $0.0018\text{--}0.0025 \text{ s}^{-1}$ Garcia-Nieto et al.(2018); peaks observed in suburban Melbourne, Australia, were approximately $0.0015\text{--}0.0020 \text{ s}^{-1}$ Ryan et al.(2018). Our North China site values are slightly higher than these sites, possibly reflecting the stronger HONO precursor (NO_2) load and unique photochemical environment in North China. (3) Regional differences: The text has already pointed out that the peak at South China sites (e.g., GZ_DXC) can reach $\sim 0.0030 \text{ s}^{-1}$, which is higher than in North China. This is consistent with the trend of higher $J(\text{HONO})$ observed in the Guangzhou area by Song et al.(2024), which may be attributed to higher humidity in South China promoting heterogeneous formation of HONO.

15. Lines 652-654: How were the CNEMC ground stations selected for comparison?

Re: Thank you for your comments. We briefly mentioned in the manuscript “Site pairs were selected following the spatial representativeness criteria of Song et al.(2023)”, but the description can indeed be more specific. The selection of CNEMC sites followed these principles: (1) Distance proximity: Prioritize selecting the CNEMC national control station geographically closest to our hyperspectral site. We set a maximum distance threshold (usually within 10–15 km, see Table S1 in the Supplement for details) to ensure that the two sites are in a similar urban/regional environmental background, reducing the impact of spatial heterogeneity. (2) Environmental consistency: Referring to the method of Song et al.(2023), we

looked not only at distance but also used satellite remote sensing data (such as land-use type, nighttime light index) and meteorological data to confirm that the candidate CNEMC site and our site are comparable in terms of land-use type (e.g., both urban areas or both suburban areas) and built-up area density. (3) Data availability: Ensure that the selected CNEMC site has continuous, valid O₃ surface concentration data during the comparison period (2021–2024).

We have expanded the sentence in the revised manuscript to: “Site pairs were selected following the spatial representativeness criteria of Song et al.(2023). Specifically, we prioritized the nearest CNEMC station within a maximum distance of ~10–15 km (detailed in Table S1) and verified environmental consistency between the paired sites using land-use and satellite-derived products, ensuring that both sites sampled comparable urban or suburban atmospheric conditions.”

16. Lines 642-661: The validation section only presents comparative validation for O₃ data and does not cover HONO data. Is there any independent validation for HONO data (e.g., comparison with other instruments or methods)? If so, it is suggested to add it; if not, it is suggested to explain the reason.

Re: Thank you for your comments. The reviewer points out an objective limitation. Within the 22 sites and time period covered by this study, we lack on-site in-situ instruments (such as tower-based HONO analyzers, etc.) that are synchronized with MAX-DOAS observations and can be used for independent validation of HONO vertical profiles. This is also a common challenge currently faced in the global field of HONO vertical observation, because HONO is extremely unstable, in-situ measurement techniques are complex, and it is difficult to achieve vertical profiling. Therefore, we cannot perform direct validation like we did for O₃. However, we enhance our confidence in the reliability of the HONO data through the following indirect methods: (1) Validation of the retrieval method: The DOAS retrieval settings and OEM profile retrieval framework we used have been applied to HONO retrieval in multiple previous studies and have been fully validated through testing on simulated data and comparison with samples of known concentrations (e.g., Liu et al., 2022; Song et al., 2023; Xing et al., 2019, 2021, 2023). (2) Consistency with O₃ retrieval results: HONO and O₃ use the same observation geometry, spectral processing workflow, and retrieval algorithm. The O₃ retrieval results have been well validated through comparison with TROPOMI and CNEMC (R=0.62, 0.66), which indirectly supports the reliability of the entire retrieval workflow (including HONO) when processing real atmospheric spectra. (3) Rationality of HONO vertical and diurnal variation characteristics: As shown in the results in the text, the HONO profiles we obtained (high near the surface, decreasing sharply with altitude) and diurnal variation (high in early morning, low in afternoon) are completely consistent in pattern with a large number of existing HONO observation studies based on different methods (e.g., Meng et al., 2020; Xuan et al., 2024, etc.), without showing anomalous physical signals.

17. Lines 658-660: Based on correlations of $R = 0.62$ and $R = 0.66$, the conclusion is that these validations “confirm the reliability” of the dataset. It is recommended to use more prudent wording, such as “confirm reasonable consistency”.

Re: Thank you for your comments. We completely agree with the reviewer’s opinion. R values of 0.62 and 0.66 do indeed indicate a good positive correlation and “reasonable consistency,” but directly concluding “confirm the reliability” is slightly absolute in wording, because correlation does not equate entirely to accuracy, and it may be affected by factors such as spatial mismatch and differences in observation principles. Using more cautious wording can more accurately reflect the significance of the validation results.

We have changed the original manuscript “Together, these two independent validations confirm the reliability of the dataset used in this study.” to: “Together, these two independent validations demonstrate reasonable consistency and provide confidence in the dataset used in this study.”

18. Lines 662-667: Figure 11c and 11d show site-specific correlations. It is recommended to briefly mention the names of the sites with the worst and best correlations in the text and analyze the reasons (e.g., complex terrain or excessive distance for comparison).

Re: Thank you for your comments. This is a very good suggestion for detailed analysis. Based on the plots in Figure 11c and 11d (the distribution of points can be seen in the original figure), we can conduct the following analysis: (1) Comparison with TROPOMI: The sites with the best correlation are usually those located on plains, away from the coastline, and with relatively uniform local pollution (e.g., WD in North China, LA in East China). Sites with potentially poorer correlation include: GZ_TM (located on a mesa in Guangzhou, high altitude, surrounded by complex terrain, where satellite pixels mix clean air from the summit with urban pollution at lower levels); SXU (located in the Taihang Mountains, steep terrain, where the satellite pixel (7×5.5 km) may cover air masses with huge differences between the summit and the valley). (2) Comparison with CNEMC: The sites with the best correlation are usually those where the CNEMC station is closest and located in the same homogeneous urban area (e.g., the CAMS site in Beijing and the nearest CNEMC station). Sites with potentially poorer correlation may include: SJZ_LC (located in the suburbs of Shijiazhuang, where the nearest CNEMC station may be in the main urban area, creating an urban-rural difference); TS (a high-altitude background site, where any comparison with a low-altitude CNEMC station has a fundamental environmental difference, so the correlation should be the lowest).

19. Lines 675-681: The summary emphasizes the extensiveness of the dataset. It is recommended to supplement the limitations of the dataset in terms of time span (e.g., limited to 2021–2024) so readers can

make a comprehensive assessment.

Re: Thank you for your comments. Thank you to the reviewer for proposing this balancing suggestion. A complete summary should showcase strengths while candidly discussing limitations. The time span of the dataset (2021–2024) does indeed bring some potential limitations: (1) Limited long-term trend analysis: 3–4 years of data are insufficient to reliably identify and quantify interannual variation trends in atmospheric components (such as O₃) driven by climate change or long-term emission reduction policies; such analysis usually requires a decade or longer time series. (2) May not cover extreme climate years: 2021–2024 may not have experienced certain extreme climate years (e.g., historically high-temperature drought years), so the response relationships of photochemical intensity to meteorological conditions derived based on data from this period may need to be cautiously extrapolated when applied to extreme scenarios. (3) Historical representativeness of sites: The data from some sites (especially those with short operating times) may be incidentally affected by specific anomalous meteorological events or emergencies in certain years, and their “climatological” representativeness needs more time to solidify.

We have added the following limitation discussion at the end of the summary section in the revised manuscript, after listing the application prospects: “However, it is important to note the limitations of the current dataset. The time span (2021–2024) limits the capacity for robust analysis of long-term interannual trends driven by climate change or policy shifts. The observed photochemical regimes may not fully represent conditions during extreme climatic years outside this period, and the climatological representativeness of sites with shorter operational histories requires continued data accumulation.”

20. Lines 700-709: Five main applications of the dataset are listed. It is recommended to add a sixth: the dataset plays an important role in assessing uncertainties in vertical parameterization schemes in atmospheric chemical mechanisms.

Re: Thank you for your comments. We completely agree and strongly support the reviewer’s proposed sixth application. This is indeed an extremely important and cutting-edge application direction. Vertical parameterization schemes in chemical transport models (such as boundary layer turbulent mixing, variation of dry deposition rates with altitude, vertical distribution of heterogeneous reactions, etc.) are one of the main sources of uncertainty in model simulations. Our high-resolution (~100 m) vertical profile data provides a direct, unique “true value” benchmark for evaluating and improving these parameterization schemes. For example: the measured vertical gradients of HONO and O₃ can be used to constrain and evaluate the parameterization of vertical turbulent diffusion coefficients in models. The measured and simulated vertical profiles of J(HONO) and J(O(¹D)) can be compared to test whether the vertical representation of aerosol-radiation interaction and photolysis rate calculations in the model is reasonable.

The OH production rate data at different altitudes can be used to verify whether the response of chemical mechanisms in the vertical direction in the model is correct.

Therefore, adding this point will significantly enhance the scientific value articulation of the dataset. We have added a sixth point after the original fifth point in the application list in the revised manuscript: “(6) serving as a critical benchmark for assessing and reducing uncertainties in vertical parameterization schemes (e.g., turbulent mixing, photolysis rates, heterogeneous reactions) within atmospheric chemical transport models.”

Referee #2

This manuscript presents and publicly releases a valuable dataset derived from the Chinese Hyperspectral Vertical Remote Sensing Network, featuring vertical profiles of O₃ and HONO acquired from 22 representative sites between 2021 and 2024. This dataset fills a critical gap in the long-term, vertical observations of key photochemical species over China, holding significant scientific value for understanding the evolution of tropospheric oxidative capacity. Overall, it represents a high-quality data paper. However, several details in the manuscript still require further refinement to enhance the overall quality and readability of the paper.

1. Lines 85-86: The word “generally” in “but generally lacks observations of key photochemical precursors such as HONO and volatile organic compounds (VOCs)” could be ambiguous. It is suggested to change to “but lacks observations of key photochemical precursors such as HONO and volatile organic compounds (VOCs)”.

Re: Thank you for your comments. We completely agree with your revision suggestion. The word “generally” is indeed ambiguous and might mislead readers into thinking that some sites have these observation capabilities, whereas in reality, current CNEMC sites generally do not include routine monitoring of HONO and VOCs. To make the expression more accurate, objective, and unambiguous, we have revised the original manuscript to: “...but lacks observations of key photochemical precursors such as HONO and volatile organic compounds (VOCs)...” This revision makes the meaning more definitive and aligns with the actual situation.

2. Lines 120-121: “the contribution of HONO photolysis to boundary-layer OH” could be changed to “the contribution of HONO photolysis to the boundary-layer OH budget” for greater precision.

Re: Thank you for your comments. In photochemical research, “OH budget” is a very rigorous and standard term, specifically referring to the quantitative balance between the sources and sinks of OH radicals. Using “boundary-layer OH budget” more accurately conveys our scientific objective of evaluating the proportion of HONO photolysis in the OH generation process compared to simply using “boundary-layer OH”. We have modified it according to your suggestion. The original text has been modified to: “the contribution of HONO photolysis to the boundary-layer OH budget”.

3. Lines 186-187: The manuscript mentions a “standardized instrument configuration”. Please explicitly state whether the spectrometers and telescopes used at all 22 sites are of the exact same brand and model.

Re: Thank you for your comments. This is a very critical technical question. The hardware consistency of

the instruments is the physical foundation for ensuring the comparability of multi-site data. We have explicitly supplemented and clarified in the revised manuscript: The spectrometers and telescopes used at all 22 sites in this network are indeed of the exact same brand and model. Specifically, all sites were equipped with high-resolution fiber-optic spectrometers of the same model and telescope systems based on the same optical design (right-angle prism + plano-convex lens). Before deployment to each site, all instruments underwent unified wavelength calibration and radiometric calibration in the laboratory to ensure consistency among the instruments.

4. Line 194: The elevation scanning sequence includes 1° , 2° , ..., 90° . Low elevation signals (e.g., 1°) are susceptible to obstructions, during the processing, were strict obstruction checks performed for low-elevation observations at all sites? If obstructions were present, were the relevant data excluded?

Re: Thank you for your comments. Thank you for raising this question, which shows rich practical experience. Low-elevation observations are indeed highly susceptible to obstruction by buildings, trees, or terrain, leading to abnormal optical paths and subsequently affecting retrieval results. We implemented a strict obstruction checking procedure in our data processing workflow: (1) Pre-deployment assessment: During the initial site construction, we used topographic maps and on-site inspections to ensure there were no obvious obstructions in the telescope's field of view (especially in low-elevation directions). (2) Software auto-screening: In routine data processing, we analyzed the variation in radiation intensity of low-elevation (especially 1° and 2°) spectra. If we found drastic jumps or abnormal attenuation in spectral intensity for non-meteorological reasons (usually manifesting as scattered light intensity lower than theoretically expected), the system would automatically flag it as "suspected obstruction." (3) Manual review and exclusion: For data flagged as such, we conducted manual review in conjunction with the site's surveillance photos and logs. Once an obstruction was confirmed, the low-elevation data from that scanning cycle were strictly excluded and did not participate in subsequent DOAS fitting and profile retrieval.

5. Line 195: "The integration time at each elevation was 1 min" refers to the integration time for observation at each elevation angle. It is suggested to change to "The integration time at each elevation angle was 1 min".

Re: Thank you for your comments. We agree with your suggestion. Adding the word "angle" eliminates any potential ambiguity between "elevation" and "azimuth" making the expression more rigorous. We have modified it to: "The integration time at each elevation angle was 1 min".

6. Line 197: "The instruments also operated at night to record dark current...". This phrasing might mislead

readers into thinking the instruments were conducting routine atmospheric composition observations at night. It is recommended to explicitly state that nighttime operation was strictly for instrument calibration and did not produce scientific data.

Re: Thank you for your comments. Thank you very much for pointing out this potential pitfall in the wording. MAX-DOAS technology relies on scattered sunlight; it cannot retrieve atmospheric compositions at night, and the original phrasing might indeed mislead non-specialist readers. We have restructured the original sentence to explicitly distinguish between “observation” and “calibration”: “For instrument calibration purposes only, the instruments operated at night to record dark current and electronic offsets. No scientific atmospheric data were derived from nighttime measurements.” With this revision, the logic is very clear and avoids misleading readers.

7. Line 207: The manuscript mentioned that the zenith spectrum (90°) was used as the reference. Please clarify whether the reference spectrum is from the same scanning cycle or if a fixed reference was used.

Re: Thank you for your comments. The zenith reference spectrum we use is the 90° elevation spectrum from the same scanning sequence as the low-elevation spectrum to be retrieved. This is a standard practice in MAX-DOAS retrieval, known as the “Sequential Reference method.” Its advantage lies in: being able to maximally cancel out changes in solar radiation intensity, instrument response drift, and slow-varying absorption contributions from the upper atmosphere (stratosphere and above) within a short period (approximately a 12-minute scanning cycle). If the time interval between the zenith spectrum and the low-elevation spectrum within the same sequence does not exceed a few minutes, these “slow-changing” factors can be considered identical, and thus are effectively eliminated during the differencing process, highlighting the differential absorption signals brought by the lower atmosphere. We do not use an averaged zenith spectrum for the day or a zenith spectrum from a specific time interval, as that would introduce uncertainties due to changes in solar zenith angle and optical path differences.

8. Line 268: In “More than \sim 85% of the sites operated for over one year”, “ \sim ” indicates an approximation, which is slightly redundant when used with “more than”. It is suggested to change to “Over 85% of the sites operated for more than one year”.

Re: Thank you for your comments. Your logic is very rigorous. “More than” itself already implies a certain degree of approximation or a lower limit; superimposing the tilde “ \sim ” indeed appears semantically redundant and unprofessional. We have adopted your suggestion and modified it to: “Over 85% of the sites operated for more than one year...”, making the manuscript more concise and crisp.

9. Line 335: Please pay attention to the subscripts for NO₂; it should be written as “NO₂”. Please check the full manuscript to ensure all instances of NO₂ are written correctly.

Re: Thank you for your comments. We apologize for this formatting oversight. Standardized writing of chemical formulas is a basic requirement for scientific papers. We have conducted multiple thorough searches and replacements throughout the manuscript to ensure that all instances of “NO₂” (including in the main text, figure captions, tables, etc.) have been correctly replaced with the subscripted format “NO₂”. At the same time, we took this opportunity to check the formats of other chemical formulas (such as O₃, HONO, O₄, etc.) to ensure consistent and standardized formatting throughout the manuscript.

10. Line 412: “the pronounced O₃ enhancements observed at 3–4 km at sites such as CQ, GZ_TM and SUIST” – here “SUIST” should be “SUST”. Please verify.

Re: Thank you for your comments. You are absolutely correct; this is indeed a typo. “SUIST” does not exist; the correct site abbreviation should be “SUST” (Southern University of Science and Technology). We have corrected “SUIST” to “SUST” in the text and conducted a second check of all site abbreviations throughout the manuscript, confirming no other similar errors.

11. Line 543: The manuscript reads “reaching 1.0×10^4 – 5.5×10^4 ppb·s⁻¹”. This should likely be 10^{-4} . It appears to be a typographical error. Please verify and correct.

Re: Thank you for your comments. We are extremely grateful that you keenly spotted this severe numerical error. Your judgment is completely accurate; a negative sign was missing from the exponent in the original manuscript, resulting in the value being magnified by 8 orders of magnitude. Verifying by physical common sense: for OH production rate $P(\text{OH}) = J(\text{HONO}) \times [\text{HONO}]$. Typically, J is on the order of 10^{-3} s^{-1} , and near-surface HONO concentration is about 0.3–0.5 ppb, so the reasonable order of magnitude for $P(\text{OH})$ should be $10^{-4} \text{ ppb} \cdot \text{s}^{-1}$. The 10^4 in the original manuscript was purely a typo. We have recalculated and corrected all values involving OH production rates throughout the manuscript, correcting the value here to “ 1.0×10^{-4} – $5.5 \times 10^{-4} \text{ ppb} \cdot \text{s}^{-1}$ ”. We sincerely apologize for the inconvenience this elementary error caused to the reviewer during reading.

12. Line 572-573: “underscoring the near-surface confinement of both HONO and its photolytic OH production.” “its photolytic OH production” could be changed to “OH production from its photolysis” for clarity.

Re: Thank you for your comments. We agree with your suggestion. The original phrasing “its photolytic OH production,” where “photolytic” acts as an adjective modifying “OH production,” is somewhat stiff and

prone to ambiguity. Modifying it to “OH production from its photolysis” treats “photolysis” as a process, making the logical relationship clearer and the language more consistent with authentic scientific English expression habits. We have made this change.

13. Line 616: There are two periods in “Figures S29–S32..”. One should be removed.

Re: Thank you for your comments. Thank you for carefully proofreading the punctuation. This is obviously a mistake operation during typesetting. We have corrected the double period at the end of the sentence to a single period.

14. Line 643: The validation section only presents the validation of O₃ data and does not cover the validation of HONO data. Is this because there is no verifiable data for HONO, or is it due to other reasons?

Re: Thank you for your comments. The reviewer points out an objective limitation. Within the 22 sites and time period covered by this study, we lack on-site in-situ instruments (such as tower-based HONO analyzers, etc.) that are synchronized with MAX-DOAS observations and can be used for independent validation of HONO vertical profiles. This is also a common challenge currently faced in the global field of HONO vertical observation, because HONO is extremely unstable, in-situ measurement techniques are complex, and it is difficult to achieve vertical profiling. Therefore, we cannot perform direct validation like we did for O₃. However, we enhance our confidence in the reliability of the HONO data through the following indirect methods: (1) Validation of the retrieval method: The DOAS retrieval settings and OEM profile retrieval framework we used have been applied to HONO retrieval in multiple previous studies and have been fully validated through testing on simulated data and comparison with samples of known concentrations (e.g., Liu et al., 2022; Song et al., 2023; Xing et al., 2019, 2021, 2023). (2) Consistency with O₃ retrieval results: HONO and O₃ use the same observation geometry, spectral processing workflow, and retrieval algorithm. The O₃ retrieval results have been well validated through comparison with TROPOMI and CNEMC (R=0.62, 0.66), which indirectly supports the reliability of the entire retrieval workflow (including HONO) when processing real atmospheric spectra. (3) Rationality of HONO vertical and diurnal variation characteristics: As shown in the results in the text, the HONO profiles we obtained (high near the surface, decreasing sharply with altitude) and diurnal variation (high in early morning, low in afternoon) are completely consistent in pattern with a large number of existing HONO observation studies based on different methods (e.g., Meng et al., 2020; Xuan et al., 2024, etc.), without showing anomalous physical signals.

15. Lines 652-655: “Song et al. (2023b)” is cited as the criterion for site selection. For readers unfamiliar with this work, it is recommended to briefly summarize the main content of the selection criteria so that

readers can understand the spatial representativeness of the validation data.

Re: Thank you for your comments. This is a very good suggestion, helping to enhance the self-consistency and readability of the paper. Simply citing a literature without explaining the criteria would indeed cause confusion for readers when assessing the reliability of the validation results. The spatial representativeness matching criteria proposed in Song et al.(2023)mainly include the following core dimensions: (1) Distance threshold: Prioritize selecting the CNEMC national control station nearest to the MAX-DOAS site, usually requiring a distance within a few to a dozen kilometers (the specific threshold depends on the site environment, avoiding crossing large pollution source blocks). (2) Underlying surface consistency: Use satellite remote sensing data (such as land-use type maps, nighttime light data) to confirm that the candidate CNEMC station and the MAX-DOAS site are in the same type of underlying surface environment (e.g., both urban core areas, or both suburban transition zones), avoiding erroneous matching like “remote sensing in the city, ground station in the village.” (3) Exclusion of interference sources: Ensure there are no large point source emissions (such as chemical plants, thermal power plants) between the two sites, to guarantee that the air masses observed by both are homologous.

Referee #3

This study presents a dataset of vertical profiles of HONO and O₃ derived from the China Ground-based Hyperspectral Vertical Remote Sensing Observation Network. The dataset covers 22 representative sites, featuring an extended temporal span and broad spatial coverage. This dataset fills a critical observational gap and holds significant value for investigating boundary layer photochemical processes and improving our understanding of tropospheric oxidative capacity. The manuscript is well structured, with detailed methodological descriptions, comprehensive result presentation, and thorough data validation, and overall represents a high-quality data paper. However, there remains room for improvement in terms of clarity of expression, logical rigor, completeness of methodological details, and adherence to formatting conventions. Specific comments and suggestions are provided below to further enhance the quality and readability of the manuscript.

1. Line 23: The phrase “primary source” is somewhat absolute. OH production involves multiple pathways; consider revising to “one of the primary sources” or specifying conditions (e.g., polluted boundary layer).

Re: Thank you for your comments. We completely agree with your opinion. Although HONO photolysis is indeed the main source of OH under specific conditions (e.g., early morning in a polluted boundary layer), considering that there are multiple pathways for OH production in the atmosphere, such as O₃ photolysis and VOC photolysis, using “primary source” is indeed too absolute. We have revised the sentence in the revised manuscript to: “Photolysis of HONO and O₃ in the troposphere is one of the primary sources of OH radical and a fundamental control on atmospheric oxidative capacity.”

2. Lines 57-58: The statement “ozone (O₃)... has continued to increase” is overly absolute. It is recommended to add qualifiers such as “in some regions” or “on average” to more accurately reflect the complex trends of ozone pollution in China.

Re: Thank you for your comments. Thank you for the correction. The trend of near-surface ozone in China has significant regional heterogeneity; for example, some coastal areas or regions with significant PM_{2.5} reductions may show different trends. The original expression was indeed too general. We have modified it to: “In contrast, ozone (O₃)—a secondary pollutant and a major atmospheric oxidant—has continued to increase on average in economically developed regions such as the Beijing–Tianjin–Hebei area...”, to more accurately reflect scientific facts.

3. Lines 97-98: The word “pronounced” in “preclude resolving the pronounced diurnal variability” is somewhat subjective. It is suggested to replace it with more objective terms like “strong” or “fine-scale”.

Re: Thank you for your comments. We agree with your suggestion. The word “pronounced” carries a relatively strong subjective tone, while “fine-scale” more accurately describes the shortcomings of satellite observations in terms of spatiotemporal resolution. We have revised the sentence to: “...preclude resolving the fine-scale diurnal variability and vertical structure of O₃ and HONO”.

4. Lines 117-118: In “to quantify the altitude-dependent production of OH radicals,” the term “altitude-dependent” might be ambiguous (dependent on altitude vs. varying with altitude). It is recommended to change it to “altitude-resolved” or “vertical variations in.”

Re: Thank you for your comments. Your understanding is very precise. “Altitude-dependent” in mathematics or physics might be misunderstood as “dependent on altitude” (i.e., a certain parameterization scheme depends on the altitude variable), whereas our purpose is to describe the “resolution of production rates varying with altitude.” We have adopted your suggestion and modified it to: “The primary objective is to resolve the vertical structure of HONO and O₃ and to quantify the altitude-resolved production of OH radicals from their photolysis.”

5. Lines 122-124: The order of region names “North, East, South, Central, and Southwest China” is not entirely consistent with the order presented later in Table 1 and the main text (e.g., Southwest China appears after South China in Table 1). It is recommended to unify the listing order of region names throughout the article.

Re: Thank you for your comments. Thank you very much for pointing out this inconsistency. Upon verification, the order in Table 1 is North, East, Southwest, South, Central. To maintain consistency throughout the manuscript, we have unified the order of mentioning these five regions throughout the text, adjusting them to the order consistent with Table 1: North, East, Southwest, South, and Central China.

6. Lines 146-148: In “stations at the Chinese Academy of Meteorological Sciences (CAMS1, CAMS2) and the University of Chinese Academy of Sciences (UCAS), located in and around Beijing...”, the phrase “in and around Beijing” is slightly ambiguous, as both stations are within the municipality of Beijing. It is recommended to change it to “located within Beijing”.

Re: Thank you for your comments. We agree with your revision suggestion. The CAMS site is located in Haidian District, and the UCAS site is in Huairou District; both are within the administrative jurisdiction of Beijing. Using “in and around” easily causes misunderstanding. We have modified it to: “In North China, stations at the Chinese Academy of Meteorological Sciences (CAMS1, CAMS2) and the University of Chinese Academy of Sciences (UCAS), located within Beijing (~100–120 m a.s.l.), characterize the heavily

urbanized and industrialized core of the Beijing–Tianjin–Hebei megacity cluster.”

7. Lines 156-157: The sentence “The summit of Mount Tai (TS; 1,500 m a.s.l.) offers vertical profiles under clean, high-altitude background conditions.” is not entirely accurate, as TS, being a major tourist destination, is subject to tourism activities and regional transport influences and is not pristine. It is recommended to change “clean” to “relatively clean background conditions”.

Re: Thank you for your comments. We completely agree with your view. As a famous scenic area, Mount Tai is indeed affected by tourism emissions and surrounding regional transport, and is by no means absolutely clean. We have changed “clean” to “relatively clean” in the manuscript to more rigorously describe its attributes as a regional background site.

8. Lines 186-200: Are the specifications of the instruments employed at each of the 22 sites consistent?

Re: Thank you for your comments. This is a very critical technical question. The hardware consistency of the instruments is the physical foundation for ensuring the comparability of multi-site data. We have explicitly supplemented and clarified in the revised manuscript: The spectrometers and telescopes used at all 22 sites in this network are indeed of the exact same brand and model. Specifically, all sites were equipped with high-resolution fiber-optic spectrometers of the same model and telescope systems based on the same optical design (right-angle prism + plano-convex lens). Before deployment to each site, all instruments underwent unified wavelength calibration and radiometric calibration in the laboratory to ensure consistency among the instruments.

9. Lines 193-194: Following “All sites employed an identical elevation scanning sequence...,” it is recommended to add a brief explanation of the scientific rationale or optimization considerations for selecting these specific elevation angles (e.g., 1°, 2°, ...90°).

Re: Thank you for your comments. This is a good suggestion; adding scientific rationale helps readers understand the observation design. We selected this set of angle sequences (especially the dense setting at low elevations) based on the following scientific considerations: the optical path at low elevations (1°-10°) mainly travels through the lower boundary layer and is extremely sensitive to the vertical gradient of near-surface pollutants; using logarithmic or quasi-logarithmic intervals (e.g., 1, 2, 3, 4, 5, 6, 8, 10) can more effectively capture the characteristic of pollutant concentrations decreasing exponentially with altitude within the boundary layer; 15° and 30° are used to cover the middle and upper boundary layer; the 90° zenith angle serves as a reference to eliminate contributions from the stratosphere and upper atmosphere. In previous studies, this was the standard elevation sequence used; we have cited previous literature as a

reference in the revised manuscript. Modified to: “All sites employed an identical elevation scanning sequence of 1°, 2°, 3°, 4°, 5°, 6°, 8°, 10°, 15°, 30°, and 90°(Liu et al., 2022; Xing et al., 2021, 2023).”

10. Line 204: In the spectral retrieval section, please specify the version number of the QDOAS software used.

Re: Thank you for your comments. Thank you to the reviewer for the reminder. The precision of the software version number is crucial for the reproducibility of the study. The version of the QDOAS software we used in the retrieval is QDOAS 3.2. We have added this information in Section 2.3 of the revised manuscript: “Ultraviolet–visible spectra measured by the ground-based instruments were analysed with the QDOAS software (version 3.2) developed by BIRA-IASB.”

11. Lines 206-208: Please clarify whether the zenith reference spectrum is the 90° spectrum from the same scanning sequence, or a daily average or zenith spectrum from a specific time period.

Re: Thank you for your comments. The zenith reference spectrum we use is the 90° elevation spectrum from the same scanning sequence as the low-elevation spectrum to be retrieved. This is a standard practice in MAX-DOAS retrieval, known as the “Sequential Reference method.” Its advantage lies in: being able to maximally cancel out changes in solar radiation intensity, instrument response drift, and slow-varying absorption contributions from the upper atmosphere (stratosphere and above) within a short period (approximately a 12-minute scanning cycle). If the time interval between the zenith spectrum and the low-elevation spectrum within the same sequence does not exceed a few minutes, these “slow-changing” factors can be considered identical, and thus are effectively eliminated during the differencing process, highlighting the differential absorption signals brought by the lower atmosphere. We do not use an averaged zenith spectrum for the day or a zenith spectrum from a specific time interval, as that would introduce uncertainties due to changes in solar zenith angle and optical path differences. We have clarified this in the revised manuscript: “For each elevation scan, the zenith spectrum (90° elevation) acquired within the same scanning sequence was used as the reference...”

12. Lines 213-214: In “using a fifth-order polynomial, allowing accurate separation of narrow-band molecular absorption,” the subject of “allowing” is unclear. It is recommended to change it to “This allows for the accurate separation...” or merge it with the preceding sentence.

Re: Thank you for your comments. Thank you for pointing out the grammatical issue. We have modified it according to your suggestion: “Broadband spectral structures were represented and removed using a fifth-order polynomial. This allows for the accurate separation of narrow-band molecular absorption.”

13. Lines 215-217: After “Strict quality control was applied: only retrievals with a root-mean-square (RMS) fitting residual below 1×10^{-3} were retained,” it is recommended to add the basis or reference for setting this specific RMS threshold.

Re: Thank you for your comments. This threshold (1×10^{-3}) is derived from common practices in the field of DOAS retrieval and the experience of extensive previous research. Excessively high RMS usually means the fitting process is severely affected by cloud interference, extreme aerosol scattering, or instrument noise, leading to unreliable retrieval results. Regarding the determination of this threshold, it has been explained in many previous studies; we cite previous literature here to explain this issue, and there are many related references (Hu et al., 2024; Ji et al., 2023; Liu et al., 2022, 2023; Song et al., 2023; Wang et al., 2019; Xing et al., 2017, 2019, 2021, 2023, 2024; Xu et al., 2021; Zou et al., 2025).

14. Lines 307-309: In “without a persistent mid-level enhancement,” the word “persistent” may not be accurate, as the dataset presents a multi-year mean state. It is suggested to change it to “without a distinct mid-level enhancement.”

Re: Thank you for your comments. Your logic is very rigorous. Multi-year averaged data smooths out transient disturbances, so “persistent” is indeed inapplicable; changing it to “distinct” better describes the characteristics under the averaged state. We have modified it to: “...without a distinct mid-level enhancement.”

15. Lines 334-336: In the sentence “This pattern reflects nocturnal accumulation driven by heterogeneous conversion... and after sunrise...,” the two clauses connected by “and” are at different logical levels. It is recommended to separate them with a semicolon or restructure the sentence.

Re: Thank you for your comments. We agree with your revision opinion. The first half describes the nighttime mechanism, and the second half describes the daytime mechanism; connecting them with “and” is indeed logically unclear. We have reconstructed the sentence using a semicolon: “This pattern reflects nocturnal accumulation driven by heterogeneous conversion of NO_2 on aerosol and ground surfaces (Liu et al., 2022; Xing et al., 2023; Xuan et al., 2025); after sunrise, enhanced solar radiation leads to the release and photochemical processing of HONO; meanwhile, morning rush-hour emissions of NO_2 and VOCs further promote HONO formation (Garcia-Nieto et al., 2018; Zhang et al., 2025).”

16. Lines 347-348: For the statement “Sites with dense vegetation or agricultural land use (LA and CF) may receive contributions from biogenic VOC-related chemistry,” it is recommended to provide a reference for research on the influence of biogenic VOCs on HONO formation.

Re: Thank you for your comments. Thank you for the reminder. Although vegetation itself does not directly emit large amounts of HONO, soil NO_x emissions associated with vegetation and heterogeneous reactions on leaf surfaces may contribute to HONO. We have added relevant references to support this statement: “Sites with dense vegetation or agricultural land use (LA and CF) may receive contributions from biogenic VOC-related chemistry, but the overall pattern still features a subdued morning maximum (Liang et al., 2017; Ryan et al., 2018b; Xue et al., 2021; Ye et al., 2023).”

17. Lines 411-412: In the sentence “The pronounced O₃ enhancements observed at 3–4 km at sites such as CQ, GZ_TM and SUIST are therefore likely linked to...,” “SUIST” should be “SUST” (the site for Southern University of Science and Technology). Please correct this.

Re: Thank you for your comments. You are absolutely correct; this is indeed a typo. “SUIST” does not exist; the correct site abbreviation should be “SUST” (Southern University of Science and Technology). We have corrected “SUIST” to “SUST” in the text and conducted a second check of all site abbreviations throughout the manuscript, confirming no other similar errors.

18. Lines 476: The phrase “using in situ concentration profiles” is incorrect, as MAX-DOAS observations are remote sensing retrievals, not “in situ” measurements. It is recommended to change it to “using retrieved concentration profiles” or simply “using concentration profiles”.

Re: Thank you for your comments. What you pointed out is very correct; MAX-DOAS belongs to remote sensing retrieval technology, and using “in situ” does cause conceptual confusion. We have modified it to: “To quantify the AOC at each site, we evaluated altitude-resolved OH production from HONO and O₃ using retrieved profiles combined with photolysis frequencies calculated by the TUV model.”

19. Lines 504-505: The manuscript states “J(HONO) exhibits a pronounced diurnal cycle, increasing during the morning (08:00–10:00) with rising solar radiation.” In fact, J values begin to rise immediately after sunrise. The fastest increase may occur during 08:00–10:00, but the peak is usually around noon. It is recommended to change it to “increasing after sunrise” for accuracy.

Re: Thank you for your comments. We agree with your scientific judgment. J(HONO) varies with solar zenith angle and begins to increase immediately after sunrise. The time limitation in the original text was too narrow. We have modified it to: “At the North China sites (CAMS1, CAMS2, UCAS, WD, SJZ_LC, SXU), J(HONO) exhibits a pronounced diurnal cycle, increasing after sunrise with rising solar radiation, peaking at midday (12:00–14:00) at 0.0020–0.0025 s⁻¹, and decreasing in the afternoon (14:00–18:00).”

20. Line 543: The manuscript states “reaching 1.0×10^4 – 5.5×10^4 ppb·s⁻¹”. For OH production $P(\text{OH}) = J(\text{HONO}) * [\text{HONO}]$, if J is taken as $\sim 10^{-3}$ s⁻¹ and HONO as 0.3–0.5 ppb, then $P(\text{OH})$ should be approximately 3×10^{-4} – 5×10^{-4} ppb·s⁻¹. The value in the text is 8 orders of magnitude larger, indicating a severe typo. Please verify and correct this.

Re: Thank you for your comments. We are extremely grateful that you keenly spotted this severe numerical error. Your judgment is completely accurate; a negative sign was missing from the exponent in the original manuscript, resulting in the value being magnified by 8 orders of magnitude. Verifying by physical common sense: for OH production rate $P(\text{OH})=J(\text{HONO}) \times [\text{HONO}]$. Typically, J is on the order of 10^{-3} s⁻¹, and near-surface HONO concentration is about 0.3–0.5 ppb, so the reasonable order of magnitude for $P(\text{OH})$ should be 10^{-4} ppb·s⁻¹. The 10^4 in the original manuscript was purely a typo. We have recalculated and corrected all values involving OH production rates throughout the manuscript, correcting the value here to “ 1.0×10^{-4} – 5.5×10^{-4} ppb·s⁻¹”. We sincerely apologize for the inconvenience this elementary error caused to the reviewer during reading.

21. Line 549: The manuscript states “exceeding 3.0×10^4 ppb s⁻¹”. This also contains an order-of-magnitude error; it should be “exceeding 3.0×10^{-4} ppb s⁻¹” or a similar magnitude.

Re: Thank you for your comments. As above, this is also a severe error in the exponent sign. We have corrected it to: “...exceeding 3.0×10^{-4} ppb·s⁻¹”.

22. Lines 615-616: The manuscript reads “at the 22 sites , and seasonal mean diurnal”. A Chinese full-width comma “ , ” is used here; it should be changed to an English half-width comma. The manuscript reads “presented in Figures S29–S32..”. There are two periods at the end of the sentence; it should be changed to one.

Re: Thank you for your comments. Thank you for pointing out the formatting issues. We have replaced the Chinese full-width comma “ , ” with an English half-width comma “ , ”, and corrected the double period at the end of the sentence to a single period.

23. Line 653: Regarding the comparison with CNEMC surface station data, please detail the methodology used to select the CNEMC stations.

Re: Thank you for your comments. We briefly mentioned in the manuscript “Site pairs were selected following the spatial representativeness criteria of Song et al.(2023)”, but the description can indeed be more specific. The selection of CNEMC sites followed these principles: (1) Distance proximity: Prioritize selecting the CNEMC national control station geographically closest to our hyperspectral site. We set a

maximum distance threshold (usually within 10–15 km, see Table S1 in the Supplement for details) to ensure that the two sites are in a similar urban/regional environmental background, reducing the impact of spatial heterogeneity. (2) Environmental consistency: Referring to the method of Song et al.(2023), we looked not only at distance but also used satellite remote sensing data (such as land-use type, nighttime light index) and meteorological data to confirm that the candidate CNEMC site and our site are comparable in terms of land-use type (e.g., both urban areas or both suburban areas) and built-up area density. (3) Data availability: Ensure that the selected CNEMC site has continuous, valid O₃ surface concentration data during the comparison period (2021–2024).

We have expanded the sentence in the revised manuscript to: “Site pairs were selected following the spatial representativeness criteria of Song et al.(2023). Specifically, we prioritized the nearest CNEMC station within a maximum distance of ~10–15 km (detailed in Table S1) and verified environmental consistency between the paired sites using land-use and satellite-derived products, ensuring that both sites sampled comparable urban or suburban atmospheric conditions.”

24. Line 660: The manuscript states “confirm the reliability of the dataset used in this study”. It is recommended to add a note regarding HONO data validation, as the text only presents validation for O₃, whereas HONO is another critical data product.

Re: Thank you for your comments. The reviewer points out an objective limitation. Within the 22 sites and time period covered by this study, we lack on-site in-situ instruments (such as tower-based HONO analyzers, etc.) that are synchronized with MAX-DOAS observations and can be used for independent validation of HONO vertical profiles. This is also a common challenge currently faced in the global field of HONO vertical observation, because HONO is extremely unstable, in-situ measurement techniques are complex, and it is difficult to achieve vertical profiling. Therefore, we cannot perform direct validation like we did for O₃. However, we enhance our confidence in the reliability of the HONO data through the following indirect methods: (1) Validation of the retrieval method: The DOAS retrieval settings and OEM profile retrieval framework we used have been applied to HONO retrieval in multiple previous studies and have been fully validated through testing on simulated data and comparison with samples of known concentrations (e.g., Liu et al., 2022; Song et al., 2023; Xing et al., 2019, 2021, 2023). (2) Consistency with O₃ retrieval results: HONO and O₃ use the same observation geometry, spectral processing workflow, and retrieval algorithm. The O₃ retrieval results have been well validated through comparison with TROPOMI and CNEMC (R=0.62, 0.66), which indirectly supports the reliability of the entire retrieval workflow (including HONO) when processing real atmospheric spectra. (3) Rationality of HONO vertical and diurnal variation characteristics: As shown in the results in the text, the HONO profiles we obtained (high near the surface, decreasing

sharply with altitude) and diurnal variation (high in early morning, low in afternoon) are completely consistent in pattern with a large number of existing HONO observation studies based on different methods (e.g., Meng et al., 2020; Xuan et al., 2024, etc.), without showing anomalous physical signals.

25. Line 681-682: The statement “represents one of the most extensive collections in China” should be verified. It is recommended to change it to “one of the most extensive publicly available collections” for greater rigor.

Re: Thank you for your comments. We accept your suggestion. There are indeed other non-public long-term observation data (e.g., internal data from certain research projects), so limiting it to “publicly available” is more rigorous. We have modified it to: “The dataset spans 22 representative sites across North, East, Central, South, and Southwest China, covering a wide range of climatic regimes and surface types, and represents one of the most extensive publicly available collections in China in terms of spatial coverage and vertical resolution of photochemical parameters relevant to OH precursors.”

References

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