We thank Dr. Matthew Johnson for his positive comments and valuable suggestions. We believe addressing these comments will help us to refine our interpretation of the results and identify areas for further clarification. Below, we respond to each comment point-by-point. Comments by the reviewer are given in black normal font, and our response to the comments is shown in blue. Newly added and modified text in the revised manuscript and supporting information (SI) is given in italics.

Comment: The authors mention unidentified processes that weaken the H_2O_2-O_3 correlation. Could they comment on plausible candidates for these processes, such as aqueous-phase reactions or nighttime chemistry? Exploring these possibilities would help clarify what additional mechanisms may need to be included in future modeling efforts.

Response: Thank you for your insightful comment regarding the unidentified processes that weaken the H_2O_2-O_3 correlation, specifically concerning the correlation between their daytime maximum peak concentrations ($r^2 = 0.19$, as shown in Figure 4). We agree with the reviewer that aqueous-phase reactions could also contribute to the weakened H_2O_2-O_3 correlation. H_2O_2 is highly soluble and can undergo various reactions in the aqueous phase (e.g., with dissolved S(IV) or through Fenton-like reactions if transition metals are present), or simply be physically partitioned into the liquid phase. O_3, being much less soluble, would be less affected. Day-to-day variations in cloud cover, fog events, or aerosol liquid water content could thus differentially impact the peak concentrations of H_2O_2 more significantly than O_3, leading to a weaker correlation between their daily maxima. While our current model incorporates a parameterized heterogeneous uptake for H_2O_2, it does not explicitly resolve detailed multiphase aqueous chemistry, which could introduce such variability.

The concentrations of H_2O_2 and O_3 carried over from the previous night set the baseline for the next day's photochemical production. If nighttime loss processes affect H_2O_2 and O_3 to different extents on different nights (e.g., due to varying NO emissions or aerosol loading/composition), this could alter the net accumulation leading to their respective daily peaks, thereby influencing the day-to-day correlation of these peak values.

In summary, while heterogeneous uptake on particles is a primary candidate we identified, the interplay of aqueous-phase processes, the nuances of nighttime chemistry impacting daytime starting conditions can all contribute to the observed weaker correlation between H_2O_2 and O_3 daily maximum concentrations.

To address this, we have revised Section 3.3 of the manuscript by adding the following text:

Line 284-287: "Additionally, aqueous-phase reactions in aerosol water or cloud droplets, facilitated by high relative humidity during the campaign, could further reduce gas-phase H_2O_2 without affecting O_3, contributing to the decoupling of their peak values. While the focus on daytime maxima limits the direct relevance of nighttime

chemistry, processes such as alkene ozonolysis or nocturnal deposition could influence background H_2O_2 levels, indirectly affecting daytime peaks."

Comment: The model initially overestimates H_2O_2 by a factor of 2.7. How robust are the RIR conclusions in light of this discrepancy? It would be helpful to discuss whether this modeling bias could influence the inferred sensitivity of H_2O_2 to different precursors. How sensitive are the model results to the assumed uptake coefficient (6×10^{-4}) for H_2O_2? Is there a justification or uncertainty range?

Response: We would like to emphasize that the heterogeneous uptake process with a coefficient of 6×10^{-4} was already incorporated into the model when conducting the RIR analysis. The factor of 2.7 overestimation refers to our initial model runs before this adjustment was made. To clarify the sequence of our modeling approach: We first ran the original model which overestimated H_2O_2 by a factor of 2.7; we then incorporated heterogeneous uptake with a coefficient of 6×10^{-4} to correct this discrepancy; the RIR analysis was performed using this adjusted model, which showed good agreement with observations. Therefore, the RIR results presented in our manuscript are derived from the optimized model that adequately reproduces the observed H_2O_2 concentrations. This means that the initial overestimation did not affect our RIR conclusions.

The following texts was added to avoid confusion:
Line 358-359: "Here it should be noted that the RIR analysis was performed using this adjusted model with H_2O_2 uptake coefficient of 6×10^{-4} that showed good agreement with observations."

The value of 6×10^{-4} was selected as it leads to the best agreement between observed and simulated H_2O_2 concentrations. It falls within the wide range of values reported in laboratory and field studies (typically 10^{-5} to 10^{-3}), which are known to be highly variable depending on factors like aerosol composition, phase, pH, and relative humidity-parameters not fully constrained in our regional simulation. We acknowledge this value carries significant uncertainty. The modeled H_2O_2 concentration is sensitive to this parameter. A sensitivity test (Figure S1) indicated that increasing γ towards values like 1×10^{-3} could make the modeled H_2O_2 concentration 19% lower than the observed H_2O_2 concentration. Given the uncertainty and sensitivity, fixing γ allows us to explore other aspects of the chemistry, but its accurate representation remains a key challenge. We have clarified the justification and acknowledged the uncertainty and model sensitivity associated with this parameter in Section 3.4.

Line 319-321: "We believe this value represents a reasonable estimate for the conditions at our sampling site, though we acknowledge that a more dynamic treatment of heterogeneous processes that accounts for variations in aerosol composition, phase state, and ambient RH would be valuable in future studies."

Comment: Does the rural Wangdu site reflect conditions across the North China Plain? How generalizable are the results?

Response: Thank you for raising this important question regarding the representativeness of the rural Wangdu site and the generalizability of our results across the North China Plain (NCP). We acknowledge that our study is based on observations from a single rural site in Wangdu, Hebei Province, which may not fully capture the heterogeneity of conditions across the entire NCP. However, we believe that the findings from this site are relevant to a broader context within the NCP for the following reasons, while also recognizing the need for further research to confirm their applicability.

First, the Wangdu site, located in Dongbaituo Village, is surrounded primarily by farmland with no significant nearby industrial facilities, making it representative of typical rural environments in the NCP. The NCP is characterized by extensive agricultural areas interspersed with small villages, and the Wangdu site shares similar land use patterns and emission profiles (e.g., lower NOx compared to urban areas, and contributions from agricultural activities and biomass burning) with many rural areas in the region. It has served as a key location for numerous large-scale campaigns studying regional air pollution in the NCP (e.g., Tan et al., 2017; Peng et al., 2021), suggesting its value for understanding conditions beyond the immediate vicinity.

Second, our results, such as the observed H_2O_2 concentrations (average of 0.62 ppb), diurnal patterns aligned with photochemical production, and the predominance of NOx-limited or transitional regimes for O_3 formation, are consistent with findings from other rural and suburban sites in the NCP. For instance, Wang et al. (2016) reported comparable H_2O_2 levels at the same site in 2014, and studies at other NCP locations, such as Mount Tai (Ye et al., 2021), show similar photochemical behaviors under low NOx conditions. Additionally, the increasing trend of photochemical pollution in rural NCP areas, as noted in our introduction (e.g., Ma et al., 2016), suggests that the processes observed at Wangdu are likely relevant to other rural areas experiencing similar shifts in pollution dynamics due to regional emission reduction policies (e.g., declining NOx and persistent VOC levels).

While the Wangdu site provides a representative case for typical rural environments in the North China Plain, spatial variability in emission sources and atmospheric conditions across the region suggests that further multi-site studies are needed to fully generalize these findings.

Comment: In Figure 3, around 19:00, H_2O_2 accounts for over 90% of total peroxides, while at 5:00, it accounts for only about 25%. Could the authors comment on the causes of this diurnal variation and the differing behavior of organic peroxides versus H_2O_2? This would enrich the interpretation of the peroxide measurements and their photochemical dynamics.

Response: At 19:00, following peak daytime photochemical activity, the highly

efficient HO_2+HO_2 pathway has led to substantial H_2O_2 accumulation. While organic peroxides (ROOH) have also been produced, the sheer rate of the HO_2 self-reaction often makes H_2O_2 the dominant peroxide species generated during intense daytime photochemistry. At this time, photochemical production is ceasing, but the accumulated H_2O_2 constitutes a large fraction (>90%) of the total peroxide.

Overnight, photochemical production has stopped entirely. Both H_2O_2 and ROOH concentrations decrease due to deposition and potential heterogeneous losses. In contrast, some longer-lived ROOH species formed during the previous day might persist relatively well for low dry deposition velocities. For instance, the dry deposition velocity of CH_3OOH is 30 times smaller than that of H_2O_2. This combination of continuous H_2O_2 loss and the persistence ROOH species leads to a relative increase in the contribution of ROOH to the (lower) total peroxide concentration observed in the early morning (~25% H2O2 vs ~75% ROOH in our case).

To address this comment, we have added the following text to the revised manuscript:

Line 259-267: "The diurnal variation in the relative contributions of H_2O_2 and organic peroxides to total peroxides, reflects their distinct production and loss mechanisms. H_2O_2 dominates (over 90%) around 19:00 due to strong photochemical production via HO_2 recombination during the day, while its contribution drops to ~25% by 05:00 due to nighttime losses (e.g., heterogeneous uptake and dry deposition) without replenishment. In contrast, organic peroxides contribute more significantly in the early morning, likely due to slower loss rates compared to H_2O_2. Organic peroxides such as CH_3OOH (methyl hydroperoxide) have much lower dry deposition rates— approximately 30 times lower than that of H_2O_2-leading to less nighttime loss and a higher relative contribution to total peroxides during early morning hours. These differences highlight the distinct photochemical dynamics and loss mechanisms of H_2O_2 compared to organic peroxides, influenced by diurnal variations in radiation, precursor concentrations, and meteorological conditions."

Comment: Line 151: Please change lagrangian to Lagrangian, as it is a proper adjective derived from Joseph-Louis Lagrange (analogous to Watt, Poisson, Newtonian, etc.).

Response: We have changed accordingly.

Comment: Typographic conventions: According to the IUPAC Green Book (3rd edition, 2007), symbols for physical quantities should be printed in italic type to distinguish them from unit symbols. Please revise:

k in line 158
r^2 in lines 258, 259, and Figure 10
T, P, and other physical quantities, if applicable elsewhere
Line 174 and elsewhere: Change O1D to O(^{1}D) to reflect the correct notation for electronically excited oxygen.

Line 177: Use a subscript for O3-i.e., O3.

Line 189: Change Hongkong to Hong Kong, the correct spelling in English.

Line 230: Change O3P to O(3P) to properly denote the electronic state of ground-state atomic oxygen.

Response: Thank you for pointing out these mistakes. All corrected as suggested.

References:

Wang, Y., Chen, Z. M., Wu, Q. Q., Liang, H., Huang, L. B., Li, H., Lu, K. D., Wu, Y. S., Dong, H. B., Zeng, L. M., and Zhang, Y. H.: Observation of atmospheric peroxides during Wangdu Campaign 2014 at a rural site in the North China Plain, Atmos Chem Phys, 16, 10985-11000, 10.5194/acp-16-10985-2016, 2016.

Ye, C., Xue, C., Zhang, C., Ma, Z., Liu, P., Zhang, Y., Liu, C., Zhao, X., Zhang, W., He, X., Song, Y., Liu, J., Wang, W., Sui, B., Cui, R., Yang, X., Mei, R., Chen, J., and Mu, Y.: Atmospheric Hydrogen Peroxide (H2O2) at the Foot and Summit of Mt. Tai: Variations, Sources and Sinks, and Implications for Ozone Formation Chemistry, Journal of Geophysical Research: Atmospheres, 126, e2020JD033975, https://doi.org/10.1029/2020JD033975, 2021a.

Ma, Z., Xu, J., Quan, W., Zhang, Z., Lin, W., and Xu, X.: Significant increase of surface ozone at a rural site, north of eastern China, Atmos. Chem. Phys., 16, 3969-3977, 10.5194/acp-16-3969-2016, 2016.