

Response to Reviewer #1

We appreciate the anonymous reviewer for the thoughtful reviews and comments. We have carefully considered the suggestions and revised the manuscript accordingly. The reviewer comments are in blue; our comments are in black, and modifications to the manuscript are in red.

General comments

This paper investigates the ozone photochemical production by a machine learning model where the key variable is formed by the volatile organic compounds. The main role is devoted to the chemical processes whereas physical processes are ignored. The measurement campaign extended during one month, from 1 to 30 April 2022 and the study site is inside the city, although the sampling site is surrounded by vegetation and close to a hill (the Namsan Mountain). In consequence, some minor changes should be introduced to determine the paper restrictions.

We sincerely thank the reviewer for emphasizing the need to define the physical, temporal, and chemical scope of the study. We agree that these boundaries should be stated explicitly, and we have revised the manuscript to address each part of this concern, as described below and in our point-by-point responses to the comments that follow. The site is surrounded by vegetation, and wind-sector analysis shows that prevailing southerly flow (large vegetation area) did not produce a BVOC-dominated mixture. Specifically, BVOCs accounted for 6.35% of measured TVOCs under southerly flow, comparable to 6.16% under easterly flow and lower than 8.71% under westerly flow, and daytime NO_x remained high under southerly flow (24.4 ppb vs. 20.0 ppb under easterly flow), consistent with an urban-influenced mixed air mass (Figure R1a; see our response to Comment 2). With regard to the temporal scope, we acknowledge that a one-month campaign at a single site cannot establish representativeness across seasons or sites in Seoul, and we have stated this limitation explicitly in the manuscript. We have also examined whether the measurements and the model response remain consistent under contrasting meteorological conditions (see our response to Comment 1; Figure S9). With regard to the physical and chemical scope, we clarify that the analysis targets the short-term relationship between ΔVOC and ΔO_3 and does not isolate local photochemical production from transport and mixing (see our responses to Comments 3 and 4). We thank the reviewer again for these valuable suggestions, which have helped us to state the scope and limitations of this study more clearly.

Comment 1

Since the measurement extension is one month, some comments about the data representativeness should be included. For instance, the authors should consider the prevailing atmospheric circulation with the suitable meteorological charts. Moreover, the authors should comment if the measurements and the model response are similar under varied meteorological conditions, such as front passages or precipitation events.

We appreciate the reviewer's request to assess representativeness across the meteorological conditions sampled during the campaign. ERA5 pressure and wind maps characterize two contrasting circulation backgrounds that span the dominant synoptic variability sampled during April 2022 (Figure S9a and S9b).

For the quantitative comparison, we divided the dataset by the median ERA5 pressure and tested model output. Observed and predicted of 18 min ΔO_3 were correlated under both higher pressure ($R^2 = 0.85$) and lower pressure ($R^2 = 0.73$), as shown in Figure S9c. The five VOCs with the largest absolute SHAP slopes remained the same in both groups and retained their slope signs. Across all 12 measured VOCs, the absolute-slope rank correlation with the full-campaign ranking was 1.00 under higher pressure and 0.986 under lower pressure. Thus, the main prediction relationship and principal VOC responses persisted across the contrasting circulation backgrounds sampled during the campaign. These results are provided as a new Supplementary Figure (Fig. S9), and a one-sentence summary has been added to Section 3.1 so the robustness demonstration is visible in the manuscript itself, not only in this response.

- **Line 72: Added** "Because the measurements were confined to one roadside site during a single month, they cannot establish representativeness across seasons or sites in Seoul."
- **Line 204: Added:** "Observed and predicted 18 min ΔO_3 remained strongly correlated in both pressure subsets, with $R^2 = 0.85$ under higher pressure and $R^2 = 0.73$ under lower pressure (Fig. S9). The same five VOCs had the largest absolute SHAP slopes in both subsets, and each retained its slope direction. This stability indicates that the inferred VOC response pattern was not limited to the more stagnant higher-pressure periods."
- **Line 186 (Supplementary) Added:**

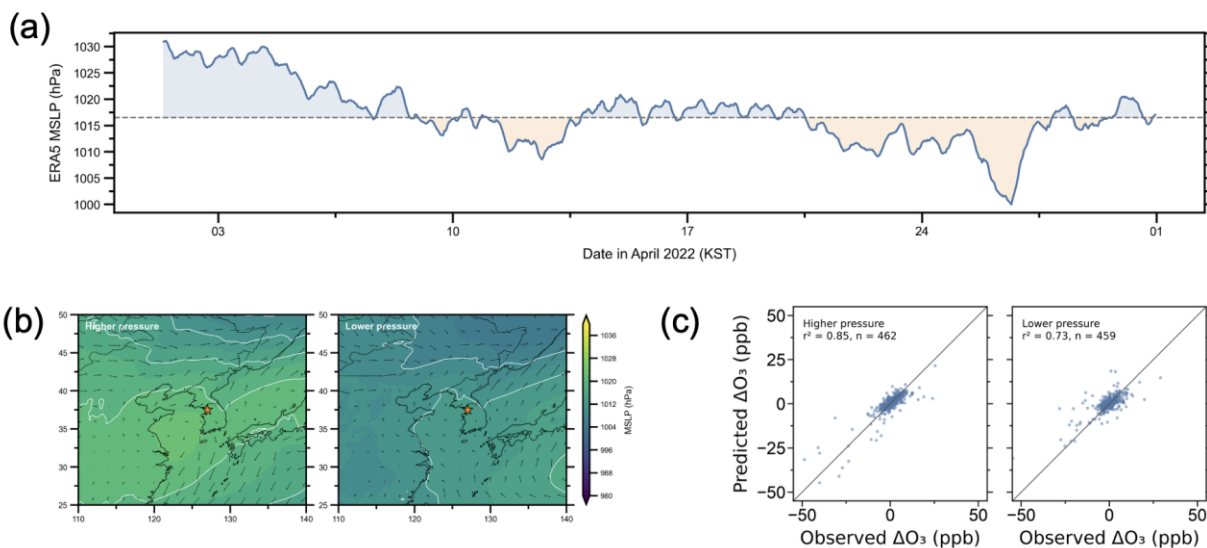


Figure S9: Meteorological robustness of the process-informed model: (a) ERA5 mean sea-level pressure at Seoul during April 2022; (b) Composite ERA5 mean sea-level pressure and 10 m winds for windows above and below the campaign-median pressure at Seoul; (c) Observed and held-out predicted 18 min ΔO_3 for the two pressure subsets. The solid line denotes 1:1 agreement, and annotations report R^2 and sample size.

Comment 2

The sampling site is close to a hill. The authors should comment if the airflow is modified by this hill. In addition, the wind rose presented in Fig. S1c shows that the prevailing wind directions come from this hill, whereas the city contribution looks like secondary. Moreover, the study site is surrounded by vegetation. Perhaps the precursor composition does not respond to that from the city, i.e. measurements may be quite local.

We sincerely thank the reviewer for raising whether Namsan Mountain and the prevailing southerly winds make the measured precursor mixture predominantly local and biogenic. The measurements do not support a BVOC-dominated mixture. BVOCs accounted for 6.35% of measured TVOCs under southerly flow, compared with 6.16% under easterly and 8.71% under westerly flow (Figure R1a). Daytime NO_x also remained high under southerly flow, with a mean concentration of 24.4 ppb compared with 20.0 ppb under easterly flow. These observations are consistent with an urban-influenced mixed air mass under southerly flow rather than an isolated vegetation-dominated air mass. Section 3.1 now reports the wind-sector composition results (Line 181). We also agree that the nearby hill may modify the local airflow and that the measurements reflect conditions at a single site; regarding airflow modification by the hill, receptor wind direction alone cannot resolve terrain-induced microscale wind fields or decouple topographic flow redirection from source influences. We have therefore stated explicitly in the manuscript that the results may not be representative of the entire city (Line 72: see also our response to Comment 1). We are grateful to the reviewer for this helpful comment.

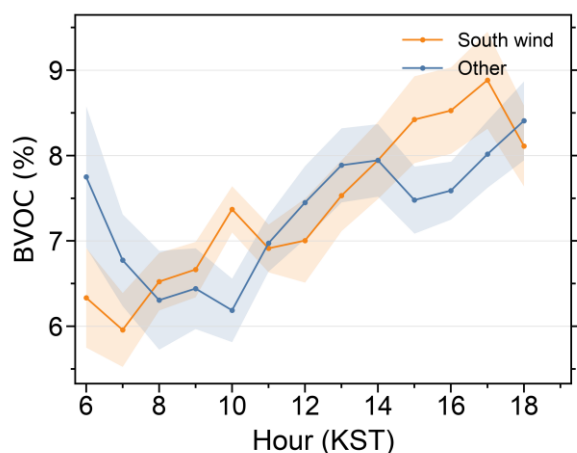


Figure R1a. Hourly mean BVOC fraction. Orange and blue show the southerly (135-225 degrees) and other wind sectors, respectively; shading shows 95% confidence intervals.

- **Line 73: Added** "Receptor wind direction alone cannot quantify topographic modification of the local wind field or uniquely apportion mountain and city sources."
- **Line 181: Added:** "The prevailing southerly sector did not correspond to a BVOC-dominated mixture. BVOCs contributed 6.35% of measured total VOCs under southerly flow, compared with 6.16% under easterly and 8.71% under westerly flow. Daytime NO_x remained high under southerly flow, with a mean concentration of 24.4 ppb compared with 20.0 ppb under easterly flow. These observations are consistent with an urban-influenced mixed air mass rather than an isolated vegetation-dominated air mass."

Comment 3

The authors present a comparison between measured and predicted O₃ deltas. Perhaps, potential readers would wonder about the reason for such comparison instead of measured and predicted concentrations.

We thank the reviewer for asking why we compare measured and predicted ΔO_3 rather than O₃ concentration. The model was designed to attribute short-term O₃ evolution associated with concurrent precursor turnover rather than to reproduce the accumulated ambient O₃ burden. We therefore defined ΔO_3 as the prediction target and paired it with ΔVOC over the same 18 min interval. Comparing measured and predicted ΔO_3 directly evaluates whether the model captures this target. In contrast, a concentration model may predict O₃ from its slowly varying background and from the accumulated effects of prior production, loss, and transport without resolving the concurrent O₃ response associated with precursor changes. Differencing reduces the influence of slowly varying background concentrations but does not isolate local photochemical production, because ΔO_3 retains contributions from chemistry, transport, and mixing. We have added this rationale to Section 2.2.2.

Line 126: Added: " ΔO_3 was used as the prediction target because the analysis examines short-term O₃ evolution associated with concurrent ΔVOC over the same 18 min interval rather than the accumulated ambient O₃ burden. This temporal differencing reduces the influence of slowly varying background concentrations but does not isolate local photochemical production, because ΔO_3 retains contributions from chemistry, transport, and mixing."

Comment 4

The authors highlight Dt=18 minutes in the text. Perhaps, they should indicate the reason, since Dt=30 minutes determines a better correlation in Fig. S7.

We thank the reviewer for asking why we retained the 18 min window although the 30 min model has a slightly higher cross-validation R². The principal VOC interpretation is stable between the two windows. The 18 and 30 min models retain the same five VOCs with the largest absolute SHAP slopes: C₁₀H₁₆, C₅H₈, C₈H₈, C₉H₁₂, and C₂H₄O. Across all 12 VOCs, the rankings by absolute SHAP slope were correlated between the two windows (Spearman $\rho = 0.762$, $p = 0.00395$). Neither interval isolates chemistry from transport and mixing. We retain 18 min because it limits temporal aggregation while still averaging high-frequency variability. The sensitivity test therefore supports using 18 min as the primary sub-hourly window without making the principal VOC interpretation contingent on that choice.

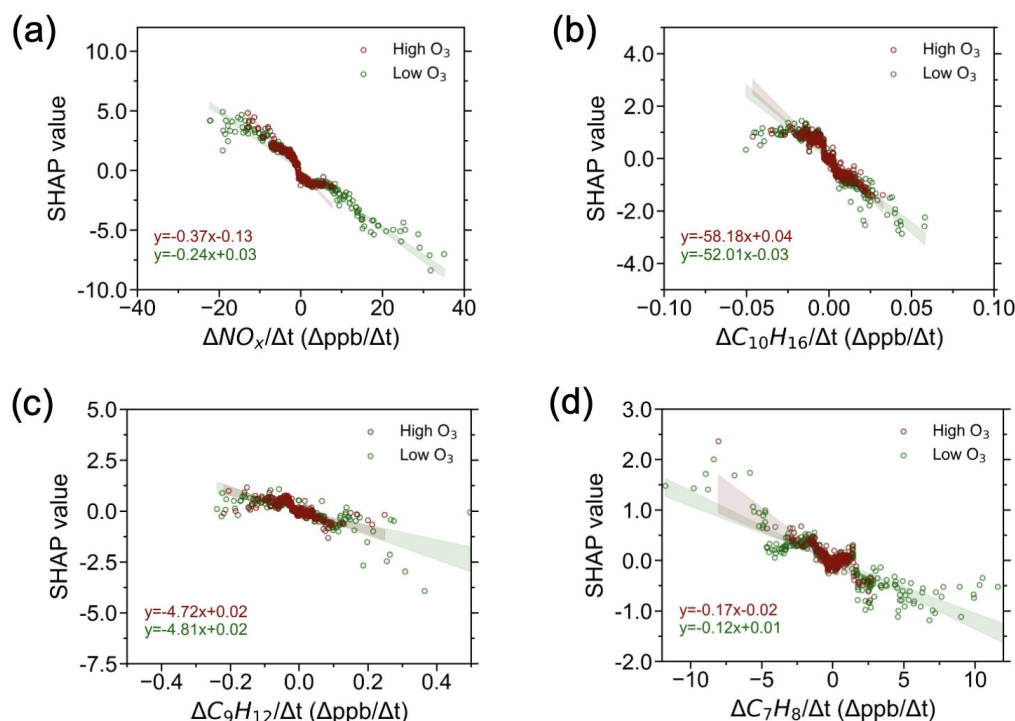
Line 130: The 18-minute integration window was rigorously determined via optimization tests (Fig. S7) to balance signal fidelity against physical transport. **After:** "We selected 18 min as the primary interval to average high-frequency variability while limiting aggregation across slower boundary-layer and transport changes (Mauder et al., 2013; Metzger, 2018). The sensitivity of the VOC attribution to this choice was evaluated against a 30 min model."

Comment 5

Some of the graphs in Fig. 5 may be misunderstood since most of the space in them is white, without dots. To see a clear result Y axes should be modified, between -5 and 5 in Fig. (b), perhaps between -7.5 and 5 in Fig. (c) and perhaps -2 and 3 in Fig. (d). These changes would allow the linear relationship to be observed and, perhaps, questioned.

We thank the reviewer for identifying that the original axis ranges obscured the populated response region. We rescaled panels (b)-(d) in Fig. 5 without changing the observations, SHAP values, regression fits, or confidence intervals. The revised ranges make both the fitted relationships and the surrounding scatter visible, allowing readers to assess the strength and dispersion of each model response directly rather than inferring linearity from the regression line alone.

Line 566: Updated Figure 5



Comment 6

Finally, the authors should determine the potential readers of this research, which is quite focused, and they should establish the way to increase them.

We thank the reviewer for asking us to define the intended readership and broaden the paper's relevance. The study is directed to researchers who interpret urban O₃ and VOC observations, assess VOC-control priorities, or apply interpretable machine learning in atmospheric science. These communities face the same attribution problem: standing concentrations may understate the role of rapidly depleted precursors. The Seoul campaign tests whether a paired comparison of concentration-based and change-based attribution can identify this bias. We revised the title to state the NO_x-saturated urban setting, distinguished the site-specific species ranking from the transferable attribution approach in the Abstract, and expanded the SHAP

explanation for readers without specialized machine-learning knowledge. The species ranking remains specific to the April 2022 roadside mixture, measured precursor suite, and sampled chemical regime. These revisions connect the Seoul demonstration to a common, testable attribution problem in urban chemistry, VOC-control research, and atmospheric machine learning without treating its species ranking as universal.

- **Line 1:** Reactivity Over Abundance: Unveiling the True Kinetic Drivers of Urban Ozone Using Process-Informed Machine Learning. **After:** Reactivity Over Abundance: Unveiling the True Kinetic Drivers of Urban Ozone Using Process-Informed Machine Learning in a NO_x-Saturated Urban Environment
- **Line 26:** Because the framework requires only sub-hourly co-located VOC and ozone observations and no prescribed mechanism, it offers a complementary empirical pathway in settings where explicit mechanism-based modeling is constrained by incomplete VOC speciation or unmeasured radical precursors. **After:** "Together, these results show that short-term precursor turnover, interpreted together with independent chemical diagnostics, can reveal kinetic O₃ drivers that are obscured by abundance-based attribution. Although the species ranking is specific to the measured precursor suite and chemical conditions sampled at this site, the framework provides a testable approach for diagnosing turnover-sensitive VOC attribution in comparable urban environments."
- **Line 99:** **Added:** "SHAP quantifies each predictor's contribution to the fitted ΔO₃ prediction and therefore identifies associations represented by the model rather than causal chemical effects. We interpreted the resulting VOC associations with the kinetic, photochemical-clock, and OBM diagnostics described below."
- **Line 381:** "Because the analysis is based on a single roadside site, a one-month spring observation period, an 18-minute integration window, and a PTR-ToF-MS suite that does not fully capture all precursor classes (notably light alkanes), further applications across seasons, source environments, and chemical regimes will be needed to test generality. The framework itself, however, requires only sub-hourly co-located VOC and ozone observations and is therefore broadly applicable wherever such data are available—including settings where explicit mechanism-based modeling is constrained by incomplete VOC speciation or unmeasured radical precursors." **After:** "The species ranking remains specific to the April 2022 Seoul roadside observations, the measured precursor suite, and the sampled chemical regime. However, the paired comparison of concentration-based and change-based attribution provides a testable diagnostic for determining whether standing concentrations underrepresent rapidly depleted precursors. The framework can be evaluated in other urban environments with collocated sub-hourly VOC and O₃ observations, while the resulting species rankings must be re-established for each precursor mixture and chemical regime."

References

Mauder, M., Cuntz, M., Drüe, C., Graf, A., Rebmann, C., Schmid, H. P., Schmidt, M., and Steinbrecher, R.: A strategy for quality and uncertainty assessment of long-term eddy-covariance measurements, *Agric. For. Meteorol.*, 169, 122–135, <https://doi.org/10.1016/j.agrformet.2012.09.006>, 2013.

Metzger, S.: Surface-atmosphere exchange in a box: Making the control volume a suitable representation for in-situ observations, *Agric. For. Meteorol.*, 255, 68–80, <https://doi.org/10.1016/j.agrformet.2017.08.037>, 2018.