

## Response to Reviewer #2

### General Comment

This manuscript introduces a process-informed machine learning framework that uses net chemical consumption (Delta VOC), rather than ambient concentration, as the predictive feature for ozone formation sensitivity, and applies it to a one-month roadside dataset (PTR-ToF-MS and trace gases) collected in Seoul in April 2022. The central premise - that concentration-based ML attribution suffers from "survivor bias" in NO<sub>x</sub>-saturated, fresh-emission regimes and thereby undervalues highly reactive precursors - is well motivated and convincingly demonstrated. The authors substantiate the ML attribution through cross-validation against an MCM-based observation-based model (radical budgets), kinetic reactivity metrics (OFP, OHR), and a photochemical-clock analysis distinguishing chemical oxidation from physical dilution.

The recovery of the kOH dependence of ozone sensitivity from observations alone, together with mechanistically interpretable outliers (the radical-termination penalty for TMB and styrene; the ozonolysis-driven radical boost for monoterpenes), represents a meaningful step toward closing the gap between data-driven modeling and kinetic theory. The finding that high-ozone episodes reflect intensified turnover of specific rate-limiting precursors rather than a regime shift carries direct implications for VOC control prioritization in NO<sub>x</sub>-saturated urban environments and is well suited to the readership of ACP. The manuscript is clearly written, and the limitations (single site, single season, incomplete precursor speciation) are candidly acknowledged. I recommend publication after the following minor points are addressed.

We thank the reviewer for the positive assessment and constructive suggestions. We address the requested points below, including the temporal-window sensitivity, measurement constraints, and the interpretation of ΔVOC as net precursor concentration change over the selected interval.

### Comment 1

**Delta VOC as a chemistry proxy.** The authors argue that the regularity of traffic emissions is captured by the 'hour of day' variable, so that the residual variance in Delta VOC represents chemical turnover (lines 117-127). However, Section 3.1 itself documents episodic, morning-confined solvent enhancements that do not follow a fixed diurnal schedule and could alias into Delta VOC. A weekday/weekend stratification, or a quantitative statement of how much Delta VOC variance is explained by the HoD variable, would strengthen this assumption.

We thank the reviewer for identifying this ambiguity in our original interpretation. For C<sub>9</sub>H<sub>12</sub> ΔVOC calculated from valid resampled bins exactly 18 min apart, its correlation with hour of day was weak ( $r = -0.10$ ;  $R^2 = 0.01$ , i.e. approximately 1% of C<sub>9</sub>H<sub>12</sub> ΔVOC variance explained by hour of day), indicating little simple linear dependence on hour of day. In a weekday/weekend comparison using the full-model SHAP values (fitted across 629 weekday and 292 weekend windows, respectively), the same five VOCs had the largest absolute slopes in the same order in both subsets (C<sub>10</sub>H<sub>16</sub>, C<sub>5</sub>H<sub>8</sub>, C<sub>8</sub>H<sub>8</sub>, C<sub>9</sub>H<sub>12</sub>, and C<sub>2</sub>H<sub>4</sub>O). Slope signs agreed for all 12 VOCs, and the absolute-slope rankings across the 12 VOCs were highly consistent (Spearman  $\rho = 0.951$ ,  $N = 12$ ). We have therefore removed the claim that hour of day isolates a purely chemical residual. The revised manuscript defines ΔVOC as short-term net precursor turnover that

integrates emissions, transport, mixing, and chemistry over the selected interval rather than as a direct measure of chemical consumption.

**Line 141:** Consequently, the remaining variance in  $\Delta\text{VOC}$  serves as a robust empirical proxy for the net chemical turnover driving local ozone production. **After:** "However, hour of day cannot account for episodic solvent emissions or weekday-dependent variability, which can remain in  $\Delta\text{VOC}$ . For trimethylbenzene ( $\text{C}_9\text{H}_{12}$ )  $\Delta\text{VOC}$  calculated from valid resampled bins exactly 18 min apart, the Pearson correlation with hour of day was -0.10, corresponding to  $R^2 = 0.01$  for this simple linear relationship. This value represents approximately 1% of the variance under a linear interpretation. We therefore use  $\Delta\text{VOC}$  as a proxy for short-term net precursor turnover rather than direct chemical consumption. Weekday and weekend subsets (evaluated across 629 weekday and 292 weekend windows, respectively) retained the same five leading VOCs in the same order ( $\text{C}_{10}\text{H}_{16}$ ,  $\text{C}_5\text{H}_8$ ,  $\text{C}_8\text{H}_8$ ,  $\text{C}_9\text{H}_{12}$ , and  $\text{C}_2\text{H}_4\text{O}$ ) and identical slope signs for all 12 VOCs, with highly consistent cross-species slope rankings (Spearman  $\rho = 0.951$ ,  $N = 12$ )."

## Comment 2

Choice of the 18-minute window. According to Fig. S7,  $R^2$  is higher at the 30-minute window (0.809 vs. 0.792). The boundary-layer argument for preferring 18 minutes is reasonable, but a brief sensitivity check showing that the key conclusions (SHAP slopes of the principal species) are stable between 18 and 30 minutes would demonstrate that the results are not contingent on this choice.

We appreciate the reviewer's suggestion and performed the requested sensitivity test. The same five VOCs had the largest absolute SHAP slopes at both 18 and 30 min:  $\text{C}_{10}\text{H}_{16}$ ,  $\text{C}_5\text{H}_8$ ,  $\text{C}_8\text{H}_8$ ,  $\text{C}_9\text{H}_{12}$ , and  $\text{C}_2\text{H}_4\text{O}$ . Their response directions were also unchanged: the slopes were negative for  $\text{C}_{10}\text{H}_{16}$ ,  $\text{C}_5\text{H}_8$ ,  $\text{C}_8\text{H}_8$ , and  $\text{C}_9\text{H}_{12}$ , and positive for  $\text{C}_2\text{H}_4\text{O}$ . The principal-species interpretation is therefore robust to this choice of integration window.

**Line 133: Added:** "The same five VOCs had the largest absolute SHAP slopes at both 18 and 30 min:  $\text{C}_{10}\text{H}_{16}$ ,  $\text{C}_5\text{H}_8$ ,  $\text{C}_8\text{H}_8$ ,  $\text{C}_9\text{H}_{12}$ , and  $\text{C}_2\text{H}_4\text{O}$ . Their response directions were unchanged, with negative slopes for  $\text{C}_{10}\text{H}_{16}$ ,  $\text{C}_5\text{H}_8$ ,  $\text{C}_8\text{H}_8$ , and  $\text{C}_9\text{H}_{12}$  and a positive slope for  $\text{C}_2\text{H}_4\text{O}$ ."

## Comment 3

Interpretation of isoprene. Given that strong daytime emissions can yield positive Delta VOC even during active oxidation, the explanation for the model's high isoprene sensitivity (detection of deviations from the expected accumulation rate) is plausible but remains qualitative. I encourage the authors to elaborate briefly in the main text, and to note there that isoprene was excluded from the linear fit in Fig. S8.

We thank the reviewer for requesting a clearer interpretation of isoprene. Because light- and temperature-dependent emission can increase concurrently with oxidation, positive isoprene  $\Delta\text{VOC}$  does not exclude active chemical loss. The model response can therefore be interpreted only as an association between departures from the recurring daytime isoprene pattern and fitted  $\Delta\text{O}_3$ , not as an observed isoprene consumption rate. This emission-oxidation covariance also makes isoprene non-comparable with the predominantly primary anthropogenic species used to summarize the cross-species  $\text{kOH}$ -SHAP relationship. We now state this boundary in the main text and explicitly identify isoprene as excluded from the linear fit.

- **Line 290:** This suggests that the model successfully detects deviations from the expected accumulation rate—identifying moments where rapid chemical loss competes with strong emissions. **After:** "For isoprene, light- and temperature-dependent daytime emissions can increase concurrently with oxidation, so positive  $\Delta\text{VOC}$  does not exclude active chemical loss. Its SHAP response therefore represents an association between departures from the recurring daytime pattern and fitted  $\Delta\text{O}_3$ , rather than a measured isoprene consumption rate. We excluded isoprene from the cross-species fit in Fig. 4a and Fig. S8 because this emission-oxidation covariance makes its response slope non-comparable with those of the predominantly primary anthropogenic VOCs."
- **Line 529 (Figure captions) and 558: Added:** "Isoprene is shown in (a) but excluded from the regression fit due to concurrent emission-oxidation covariance."

#### Comment 4

$\text{NO}_2$  measurement and the HONO constraint. The Thermo 42i employs a molybdenum converter, which is known to exhibit positive  $\text{NO}_2$  interference from  $\text{NO}_x$  species in roadside environments. Please briefly discuss the potential implications for the titration-sensitivity interpretation and for the OBM constraint of  $\text{HONO} = 2\%$  of  $\text{NO}_x$ , and, if available, report a sensitivity test of the OBM results to the HONO assumption.

We thank the reviewer for raising the  $\text{NO}_2$  interference and HONO constraint. We tested HONO at 0%, 2%, and 4% of  $\text{NO}_x$ ; although the absolute initiation fluxes changed, the toluene-to-acetone direct  $\text{RO}_2$  initiation-flux ratio remained approximately 29. The relative pathway comparison is therefore insensitive to the tested HONO assumption. The short-term  $\text{O}_3$  suppression associated with fresh  $\text{NO}$  remains consistent with titration, but we do not interpret the magnitude of the  $\text{NO}_x$ -related response as interference-free because the molybdenum converter may positively bias absolute  $\text{NO}_2$  and derived  $\text{NO}_x$ .

- **Line 81: Added** "The 42i molybdenum converter also responds to oxidized nitrogen species ( $\text{NO}_z$ ), which can positively bias absolute  $\text{NO}_2$  and derived  $\text{NO}_x$ . We therefore interpret the magnitude of  $\text{NO}_x$ -normalized quantities and  $\text{NO}_x$ -related model responses with this measurement interference in mind."
- **Supplementary Line 48: Added** "Because HONO was not measured, sensitivity cases with HONO fixed at 0%, 2%, and 4% of  $\text{NO}_x$  were also evaluated. Absolute direct radical-initiation fluxes varied across these cases, whereas the toluene-to-acetone direct  $\text{RO}_2$  initiation-flux ratio remained approximately 29. This comparison supports the relative oxidation-pathway contrast for these two constrained VOCs; it does not establish an invariant absolute radical budget or  $\text{P}(\text{O}_3)$ ."

#### Comment 5

Unmeasured reactive alkenes. The authors note the absence of light alkanes (ethane, propane), but light alkenes (e.g., ethene, propene) are likewise not quantified by PTR-MS and can contribute substantial OH reactivity at roadside sites. I suggest stating explicitly that the attribution is conditional on the measured precursor suite, with alkenes included in this caveat.

We thank the reviewer for identifying this omission. Ethene, propene, and other light alkenes were not quantified by our PTR-MS configuration, so their direct contributions to OH reactivity and subsequent peroxy-radical formation are absent from the model inputs. If these unmeasured compounds covary with

measured species, part of their associated signal may also be assigned to included predictors. We have therefore clarified that the reported attribution compares relative importance within the measured precursor suite and does not constitute a complete ranking of all reactive VOCs or control candidates present at the site.

**Line 92:** "Finally, it must be noted that certain key precursors, particularly light alkanes (e.g., ethane, propane), were not accurately quantified by the specific PTR-MS configuration used and are absent from model inputs." **After:** "The PTR-MS configuration did not quantify light alkanes (e.g., ethane and propane) or light alkenes (e.g., ethene and propene). Their OH reactivity and subsequent peroxy-radical production are therefore absent from the model inputs. The reported attribution is conditional on the measured precursor suite, and covariance with unmeasured VOCs may contribute to the signal assigned to included predictors."

#### Comment 6

Application of KORUS-AQ (2016) ratios. The fixed ethylbenzene/xylene split (0.366) and the isomer-weighted kOH values are derived from the 2016 campaign and applied to 2022 observations. A sentence or two on the uncertainty introduced by possible changes in solvent regulations and fleet composition would be appropriate.

We appreciate the reviewer's request for clarification. A study published after our original submission provides a direct check on the measurements in Seoul during May-June 2022. Kang et al. (2026) reported ethylbenzene/(m,p-xylene) = 0.75, close to the corresponding KORUS-AQ value of  $432/538 = 0.803$ . The agreement supports a similar relative abundance of ethylbenzene and m,p-xylene in the two springtime Seoul datasets despite intervening changes in solvent use and fleet composition. Kang et al. (2026) did not report o-xylene, so the 2022 observations cannot independently reproduce the three-component ethylbenzene fraction of 0.366. We have added this evidence and its boundary to Section 3.1. The 0.366 allocation affects the ternary coordinates and post hoc effective kOH, but not the measured total C<sub>8</sub>H<sub>10</sub> time series or its XGBoost/SHAP attribution. For the post hoc kinetic comparison, we also distinguish the central constituent-weighted effective kOH of  $13.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from the conservative component range of  $7.0\text{-}23.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Line 189:** Because PTR-ToF-MS cannot chemically resolve C<sub>8</sub>H<sub>10</sub> isomers, ethylbenzene was differentiated from xylenes using a fixed ratio (0.366) derived from speciated measurements during the local KORUS-AQ campaign (Simpson et al., 2020). **After:** "Ethylbenzene accounted for 45% of the combined ethylbenzene and m,p-xylene abundance during KORUS-AQ and 43% in Seoul in 2022, suggesting similar C<sub>8</sub>H<sub>10</sub> composition across the two campaigns (Kang et al., 2026). The value 0.366 used here is lower because it is calculated relative to total C<sub>8</sub>H<sub>10</sub>, including o-xylene. This allocation affects only the ternary diagnostic and the post hoc kOH calculation; the ML model uses measured total C<sub>8</sub>H<sub>10</sub>."

#### Comment 7

Comparison with the WHO guideline. The WHO peak-season guideline (31 ppb) is defined as the average of daily maximum 8-hour means over the peak season; comparing 83% of hourly measurements against it is not strictly consistent with the metric's definition. Please rephrase for accuracy.

We thank the reviewer for identifying the mismatch between hourly observations and the WHO metric. Across 19 days with sufficient temporal coverage, the campaign-period mean of the daily maximum 8 h O<sub>3</sub> means was 53.95 ppb. We revised Section 3.1 to report this value and the WHO peak-season guideline of 31 ppb.

**Line 177:** Crucially, 83% of hourly measurements exceeded the WHO peak-season guideline of 31 ppb (World Health Organization, 2021), highlighting the persistence of hazardous ozone levels in this NO<sub>x</sub>-saturated environment. **After:** "Across 19 days with sufficient temporal coverage, the campaign-period mean of the daily maximum 8 h O<sub>3</sub> means was 53.95 ppb. The WHO peak-season guideline for the average of daily maximum 8 h O<sub>3</sub> means is 31 ppb".

## Comment 8

Numerical consistency. The C<sub>8</sub> aromatics concentration in the main text (1.40 +/- 1.10 ppb, line 148) differs from the C<sub>8</sub>H<sub>10</sub> value in Table S1 (1.27 +/- 1.03 ppb). Please clarify the scope of the calculation (e.g., whether styrene is included) or reconcile the values.

We thank the reviewer for identifying the apparent inconsistency. The values refer to different quantities: 1.40 +/- 1.10 ppb is the sum of C<sub>8</sub>H<sub>8</sub> and C<sub>8</sub>H<sub>10</sub>, whereas 1.27 +/- 1.03 ppb is C<sub>8</sub>H<sub>10</sub> alone. We now label these quantities explicitly.

**Line 172:** While the bulk VOC composition was numerically dominated by oxygenated species (OVOCs) such as methanol and acetone (Table S1), the substantial abundance of primary aromatics, specifically toluene (4.51 ± 6.02 ppb) and C<sub>8</sub> aromatics (1.40 ± 1.10 ppb). **After:** "Oxygenated VOCs (OVOCs), including methanol and acetone, dominated the measured VOC abundance, while primary aromatics were also prominent: mean toluene was 4.51 ± 6.02 ppb and the sum of styrene (C<sub>8</sub>H<sub>8</sub>) and unresolved ethylbenzene/xylenes (C<sub>8</sub>H<sub>10</sub>) was 1.40 ± 1.10 ppb (Table S1)."

## Technical Corrections

- The axis and MAE units in Fig. S7 ("ppm") appear to be typographical errors for "ppb"; please verify.
- The toluene kOH is given as  $5.7 \times 10^{-12}$  in the main text but 5.63 in Table S2; please unify.
- Equation numbering is duplicated between the main text and the SI (both use "(1)"), and in SI Text S7 the SHAP equation is referred to as "Equation (1)" while labeled (2); please harmonize.
- Minor typographical issues throughout, e.g., missing space in "radicals(Tuazon)" (line 275); subject-verb agreement in the Fig. 4 caption ("kOH for isomeric groups are").

We thank the reviewer for identifying these inconsistencies. We verified that ΔO<sub>3</sub> and MAE were calculated in ppb and corrected the Figure S7 labels without changing any numerical results. We standardized the toluene kOH to  $5.63 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, labeled the SHAP decomposition as Equation (1), renumbered ΔX as Equation (2), numbered the supplementary OH-exposure equation as (S1), and removed

the duplicate SHAP equation from the Supplement. We also corrected additional typographical errors, including the spacing before the Tuazon et al. (1993) citation and revised the Figure 4 caption for grammatical agreement.

## References

Kang, S., Lee, M., Lee, G., Chang, L., Shin, S.-A., and Kim, J.-A.: Characteristics of Volatile Organic Compounds (VOCs) in Seoul Metropolitan during 2022 SIJAQ Campaign, *J. Korean Soc. Atmos. Environ.*, 42, 104–122, <https://doi.org/10.5572/KOSAE.2026.42.1.104>, 2026.

Simpson, I. J., Blake, D. R., Blake, N. J., Meinardi, S., Barletta, B., Hughes, S. C., Fleming, L. T., Crawford, J. H., Diskin, G. S., Emmons, L. K., Fried, A., Guo, H., Peterson, D. A., Wisthaler, A., Woo, J.-H., Barré, J., Gaubert, B., Kim, J., Kim, M. J., Kim, Y., Knote, C., Mikoviny, T., Pusede, S. E., Schroeder, J. R., Wang, Y., Wennberg, P. O., and Zeng, L.: Characterization, sources and reactivity of volatile organic compounds (VOCs) in Seoul and surrounding regions during KORUS-AQ, *Elem. Sci. Anthr.*, 8, 37, <https://doi.org/10.1525/elementa.434>, 2020.