Response to the Referee #1 for the "Insights on Ozone Formation Sensitivity in Southeast and East Asian Megacities during ASIA-AQ"

Cho et al.

We would like to thank the reviewer for their careful reading of the paper and for providing useful comments which improved the manuscript. We reply here to each reviewer comment (comment shown in italics). Blue text represents the corresponding correction in the manuscript.

Anonymous Referee #1

Comment #1: *The choice of a 750 m altitude threshold to represent near-surface conditions is reasonable and supported by vertical profiles (Fig. 2). However, the authors should test the sensitivity of this altitude to selecting another altitude and how it would impact the 4 cities considered in this study, particularly given potential vertical gradients in NO_x, VOCs, and photolysis rates. A brief sensitivity test or justification based on boundary-layer height variability would improve the methodology.*

Response #1: We thank the reviewer for this helpful suggestion. To evaluate the sensitivity of the analysis to the selected altitude threshold, we performed additional simulations using precursor constraints derived from observations below alternative altitude thresholds (500, 750, 1000, and 1500 m). This sensitivity analysis was conducted using the flight steady-state (FSS) configuration of the box model (Sect. 2.2 and SI Sect. S2). The results show that the resulting PO_x estimates are broadly consistent across the four cities for thresholds between 500 and 1000 m. Larger differences appear only when extending the threshold to 1500 m, where observations include air masses increasingly influenced by conditions above the boundary layer. These results support the use of 750 m as a reasonable threshold for representing near-surface urban air masses. The results of this sensitivity test are now provided in the Supplement (Table S3 and text), and a brief reference has been added in the manuscript. In Lines 147-148, we have revised the text to be "Inspection of precursor vertical profiles (Fig. 2) and sensitivity tests with different altitude cuts (see Supplementary Information (SI) Sect. S2) supports 750 m as a sensible and conservative choice that keeps the analysis centered on boundary-layer chemistry."

Table S3. Mean and standard deviations of precursor concentrations and simulated POx to the selected altitude threshold for the four megacities.

Location	Altitude threshold (m)	NO_x (ppbv)	O_3 (ppbv)	CO (ppbv)	VOCR (s^{-1})	PO_x (ppbv hr^{-1})
MM, PHL	500	4.26 ± 6.11	46.90 ± 13.51	210.44 ± 61.65	1.15 ± 1.32	10.58 ± 7.46
	750	3.72 ± 5.30	47.72 ± 15.19	205.53 ± 62.46	1.16 ± 1.39	10.44 ± 6.91
	1000	3.65 ± 5.24	47.28 ± 15.02	203.40 ± 62.95	1.15 ± 1.38	10.28 ± 6.80
	1500	3.49 ± 5.15	46.70 ± 14.80	199.66 ± 63.41	1.11 ± 1.36	9.77 ± 6.82
BMR, THAI	500	10.32 ± 7.92	51.91 ± 19.98	324.01 ± 87.44	1.60 ± 1.23	14.68 ± 7.33
	750	8.07 ± 7.24	58.06 ± 22.33	310.55 ± 81.66	1.45 ± 1.13	15.62 ± 6.38
	1000	6.58 ± 6.61	59.73 ± 20.62	308.52 ± 75.20	1.35 ± 1.05	14.35 ± 7.19
	1500	5.73 ± 6.40	60.22 ± 19.64	305.82 ± 75.46	1.25 ± 1.00	13.81 ± 7.47
TKMA, TWN	500	3.24 ± 2.73	64.28 ± 9.19	277.00 ± 61.20	0.98 ± 0.79	13.38 ± 4.67
	750	2.53 ± 3.03	62.58 ± 14.29	275.27 ± 102.85	0.78 ± 0.73	11.02 ± 5.63
	1000	2.09 ± 2.83	61.05 ± 14.20	260.39 ± 93.18	0.66 ± 0.65	8.86 ± 5.38
	1500	1.73 ± 2.70	56.73 ± 15.20	236.59 ± 93.46	0.56 ± 0.60	8.09 ± 5.29
SMA, KOR	500	12.01 ± 11.59	49.08 ± 8.69	256.32 ± 71.46	1.02 ± 1.23	1.36 ± 1.05
	750	10.66 ± 10.59	50.38 ± 8.75	248.60 ± 66.81	0.94 ± 1.16	1.30 ± 1.07
	1000	8.66 ± 9.57	51.84 ± 8.30	234.47 ± 63.81	0.79 ± 1.03	1.27 ± 1.06
	1500	5.33 ± 7.84	53.00 ± 7.53	204.76 ± 62.25	0.52 ± 0.81	0.73 ± 0.81

Comment #2: *Averaging observations over 1–2 h flight tracks may obscure rapid chemical transitions and plume heterogeneity, especially in high-NO_x urban environments. The authors should discuss the implications of this temporal smoothing for nonlinear ozone chemistry and whether shorter averaging windows were tested.*

Response #3: We thank the reviewer for this insightful comment. The potential impact of temporal averaging on the isopleth analysis was evaluated using the FSS box model described in Sect. 2.2 and Supplementary Sect. S2. Unlike the isopleth framework, which uses precursor concentrations averaged over each 1–2 h flight track, the FSS model treats each observation independently at 1-minute temporal resolution and diagnoses instantaneous PO_x along the flight track. As described in Lines 276–282, the PO_x values derived from the FSS model show generally good agreement with those inferred from the isopleth framework across regions (Slope: 0.83-1.2; Fig. S5). This comparison indicates that the main features of the PO_x sensitivity diagnosed by the isopleth

analysis are robust to the temporal averaging applied in the track-based approach. We have clarified this point in Lines 276-282 as following:

"In addition, as noted in Sect. 2.2, the representativeness of this isopleth-based PO_x estimation was further evaluated by comparison with PO_x simulated from ~~a flight steady-state (~~FSS~~)~~ box mode~~l, which treats each observation independently to estimate instantaneous PO=x along the flight track~~ (Sect. 2.2 and SI Sect. S2). The two approaches showed generally good agreement across regions, indicating that the key features of the inferred PO_x sensitivity are not strongly affected by the 1–2 h temporal averaging used in the isopleth framework ~~supporting the reliability of the isopleth framework for diagnosing POx sensitivity~~ (Fig. S5). Using the FSS box model results, the contributions of each O_x production or destruction term in Eq. (1) were computed and are shown in Fig. S6. City-specific PO_x budget features are discussed in Sect. 3.2."

Comment #3: *MCM is a widely accepted chemical mechanism. However, it can be biased due to the neglection of heterogeneous chemistry, for example, HO_2 uptake on aerosols, and the impact of halogens on secondary chemistry and radical budget. The authors can include a brief discussion on the direction and impact of these uncertainties.*

Response #3: We thank the reviewer for this helpful comment. The box model simulations in this study employ MCMv3.3.1, which provides a near-explicit representation of gas-phase VOC oxidation chemistry and is widely used in atmospheric box-model studies of ozone formation. Processes such as heterogeneous uptake of radicals on aerosols or halogen-mediated chemistry are not explicitly represented in this mechanism and could influence radical budgets under certain conditions. However, evaluating these processes quantitatively would require additional observational constraints (OH, HO_2, halogen species, etc.) and model development beyond the scope of the present study. To acknowledge this limitation, we added a brief statement in Lines 151-154 as following: "…, was applied to represent VOC oxidation chemistry and its role in ozone formation. Processes not represented in the current gas-phase mechanism (e.g., heterogeneous radical uptake or updated halogen chemistry) may influence radical budgets under certain conditions and therefore represent a potential source of uncertainty.

Comment #4: *"A gridded parameter space was created by scaling the observed mean mixing ratios of NO_x and total VOCs from 1 to 300%." Please clarify this scaling approach to improve reproducibility.*

Response #4: Corrected. To improve clarity and reproducibility, we have added "Total VOCs were scaled linearly in 10% increments, with all individual VOC species adjusted proportionally to preserve VOC speciation. NO_x was scaled using a step size of 0.2 in log space, while maintaining a fixed NO/NO_2 ratio." in Lines 171-173.

Comment #5: *Section 2.3 is conceptually clear but not sufficiently detailed for full reproducibility. For example, grid resolution, ridge identification algorithm, and transition-line fitting are not sufficiently specified to allow full reproducibility of the orthogonal distance metric.*

Response #5: The grid resolution has been clarified as described in Response #4. In addition, we have revised Lines 191–195 to more explicitly describe the ridge identification procedure and transition-line fitting approach. The revised text now reads: "The ridge of the PO_x surface was identified by locating the PO_x maxima along both NO_x and VOC dimensions of the grid, and the resulting ridge points were fit using a least-squares linear regression to define the transition line. Observed data points were then overlaid onto this space to quantify their position relative to the transition line and associated PO_x sensitivity regimes~~, and the transition line between NOx- and VOC-sensitive regimes was defined as the ridge that follows the direction of steepest descent of POx values.~~".

Comment #6: *Section 3.2 discusses the individual POx isopleths. However, the authors may consider adding a brief comparative discussion of regime differences across cities and times of day, as this could further strengthen the interpretation*

Response #6: We thank the reviewer for this helpful suggestion. Following this comment, we have added a new subsection (Sect. 3.2.5, "Comparative overview of PO_x isopleths across cities and times of day") to provide a concise cross-city and diurnal comparison of the PO_x isopleths.

"3.2.5 Comparative overview of PO_x isopleths across cities and times of day

Across the four megacities, the PO_x isopleths differ systematically, as reflected in differences in transition-line slopes (Table S4), the background isopleth patterns (Figs. 4a–7a and S7–S10), and the distributions of observed data points (Figs. 4b-7b).

The slopes of the transition line calculated from the PO_x isopleths range from approximately 3 to 40 across the four cities. MM shows the shallowest transition line (slope = 4.71, Table S3), followed by progressively steeper slopes in BMR (7.01) and TKMA (11.24). SMA exhibits a substantially steeper transition line (30.27), indicating a markedly different background isopleth geometry under colder conditions. In addition, a clear diurnal variation in the individual isopleths is evident primarily in MM, with larger transition slopes during morning tracks and decrease toward afternoon tracks. In contrast, BMR and TKMA show relatively minor diurnal changes within individual flights (except for RF12 Track 2), with transition-line slopes remaining broadly consistent across tracks. SMA shows no systematic diurnal pattern in the transition-line slopes.

The distributions of the observed data points further highlight differences in how each city samples on its isopleths. In MM, the morning tracks exhibit a relatively broad spread of observed

points across the NO_x–VOC space, whereas observations during later tracks become more concentrated and are largely confined to a narrow NO_x range, predominantly below 5 ppbv, on the NO_x-sensitive side of the transition line. In contrast, BMR and TKMA show a more dispersed distribution of observed points across the NO_x–VOC space, spanning a wider range of precursor conditions relative to the transition line. In SMA, the observed points also appear widely distributed in NO_x–VOC space. However, because of the substantially steeper transition line, nearly all observations fall on the VOC-sensitive side of the isopleths despite this apparent spread."

Comment #7: *The FSS model and its setup should be included in the methodology section.*

Response #7: We have revised Sect. 2.2 to explicitly describe the flight steady-state (FSS) model configuration within the methodology section as follows:

In Line 144, we have removed "~~averaged within each flight track (typically spanning ~1–2 hours per track)~~".

In Lines 169-183, we have added "For the construction of PO_x isopleths, the model was constrained over each megacity using precursor concentrations averaged within each flight track (typically spanning ~1–2 hours per track). A gridded parameter space was created by scaling the observed mean mixing ratios of NO_x and total VOCs from 1 to 300%. Total VOCs were scaled linearly in 10% increments, with all individual VOC species adjusted proportionally to preserve VOC speciation. NO_x was scaled using a step size of 0.2 in log space, while maintaining a fixed NO/NO_2 ratio. Each NO_x–VOC grid point was used as input to the box model to compute PO_x. The NO_x–VOC grid enabled simulation of a wide range of conditions, reflecting both low and high precursor levels, while holding their speciation constant.

In addition to the isopleth simulations, a flight steady-state (FSS) configuration was implemented using the same chemical mechanism and constraint strategy described above (see Supplementary Sect. S2 for details). Unlike the isopleth approach, which applies track-averaged precursor constraints to construct a gridded NO_x–VOC scaling space, the FSS simulations were performed using time-resolved in-situ observations along the aircraft track (1 minute average). For each data point, the model was run to achieve steady state using the corresponding observed constraints to diagnose instantaneous PO_x along the flight track. This configuration enables evaluation of PO_x without applying precursor scaling or track-averaging, thereby providing a complementary perspective on how the 1–2 hour averaging and scaling assumptions used in the isopleth framework influence the inferred PO_x values."

Modify title of Section 2.3 "Isopleth ~~construction~~ projection and orthogonal distance calculation"**.**

In Lines 186-188, we have removed "~~A gridded parameter space was created by scaling the observed mean mixing ratios of NOx and total VOCs from 1 to 300%. This grid enabled simulation~~

~~of a wide range of conditions, reflecting both low and high precursor levels, while holding their speciation~~"

Comment #8: *The authors state that the box model is constrained using meteorological variables and photolysis rates. Please clarify the source of these parameters (e.g., in situ aircraft measurements, radiative transfer calculations, or model-derived values), and briefly describe how they were implemented in the box model and potentially the bias associated with this.*

Response #8: Photolysis frequencies and meteorological parameters used to constrain the box model are obtained from in-situ DC-8 aircraft measurements, as noted in Line 145 and Table S2. To clarify how photolysis was implemented in the model, we added the following sentence in Lines 156-157: "In this configuration, the measured photolysis frequencies were adjusted according to the evolving solar zenith angle at 20-minute intervals."

Comment #9: *The manuscript would also benefit from a brief discussion of how uncertainties in observed NOx, VOCs, and photolysis rates propagate into POx estimates and regime classification, particularly near the transition line.*

Response #9: Measurement uncertainties of the instruments used to constrain the box model have now been explicitly summarized in Table S2 in the Supplement. To evaluate how these uncertainties propagate into the analysis, we estimated the combined uncertainty of the observed NO_x and total VOC mixing ratios and added the corresponding propagated error bars to the observational data points in the individual isopleth plots (Supplementary Figs. S7–S10).

Furthermore, to illustrate how these observational uncertainties influence the inferred PO_x reduction responses, the resulting uncertainty range has been propagated into the PO_x response curves shown in Fig. 8, where dashed lines indicate the range of possible responses associated with the measurement uncertainties in NO_x and VOC observations.

These show that the propagated uncertainty ranges do not substantially shift the observational constraints across the transition line between NO_x- and VOC-sensitive regimes. Consequently, the inferred regime classification and the relative effectiveness of NO_x versus VOC reductions remain robust within the observational uncertainty range considered in this study.

We revised the captions in Figs. S7–S10 by adding the following sentence: "Horizontal and vertical error bars represent the measurement uncertainties of NO_x and total VOC mixing ratios, respectively." In addition, "The dashed lines indicate the range of PO_x reduction responses obtained by propagating measurement uncertainties in NO_x and VOC observations." was added to the caption of Fig. 8.