Reply to comments from Referee #1

First of all, thank you for your valuable comments and suggestions. Following your comments, we attempt to clarify and improve the manuscript by eliminating, modifying, and adding several parts from/into the original text. The added or modified parts are painted in a blue color in the revised manuscript.

[General Comment]

In Kim et al., 2025, the authors add and update the halogen (Chlorine, Bromine, and Iodine) chemistry scheme in the WRF-CMAQv5.2.1 setup for the Korean peninsula region. To implement the model, they first generate new emission datasets for anthropogenic Cl, Br species and natural Iodine species for the region. They run six simulations, CTRL (no halogens), EXP_{Cl}(where chlorine reactions are updated), EXP_{Cl-Br} (where Chlorine and Bromine are updated), $EXP_{Cl-Br-I}$ (where all three species are updated), EXP_{CAM} (where Saiz-Lopez, 2014 CAM-Chem halogen scheme is used), and EXP_{CMAQ} (CMAQ model with halogen chemistry by Sarwar et al., 2015). First they compare $EXP_{Cl-Br-I}$, EXP_{CAM} and EXP_{CMAQ} against observed $ClNO_2$, Cl_2 values from the KORUS-AQ campaign at two sites, Olympic Park and Mt. Taehwa. Results show that the simulation with halogen chemistry performs better in matching observed $ClNO_2$ and Cl_2 values, although there is uncertainty for Cl_2 both in terms of the simulated values and observations. Ozone changes in response to the new halogen reactions shows compensating changes with increased formation of ozone over land and increased destruction over the oceans. Finally, the impact of the halogen scheme on OH (5% increase), HO_2 (5.3% decrease), VOCs (5.9% decrease), NOx (2.9% increase), and HCHO (1.6% increase) is discussed. I think the paper is well-written. The structure of the paper is straight-forward and easy to understand. This study highlights the importance of having a more complete halogen chemistry in chemistry models, as it affects OH, VOCs, nitrate, sulfates, PM2.5 and O_3 and there is a need to understand these changes on a regional scale. Other than some changes that clarify and improve the readability of the paper, I think this paper is suitable for publication.

[Major Suggestions]

Comment 1: Can you provide more details on the model runs and how the statistics were calculated - How long was the model run for and what is the time-period of the runs? Which period were the observations taken, (summer or winter or which months) And how typical were these observations compared to the other sites? Maybe I missed it, but can you provide a reference(s) for the campaign?

Reply: We ran the model from May 1 to June 12, 2016 with a 5-day spin-up days, from April 26 to April 30. These spin-up days are necessary to reduce the uncertainty of initial conditions (please refer to lines 102 and 129-130).

Statistical metrics were calculated using hourly modeled and observed concentrations with the formulas shown below:

$$\mathrm{RMSE} = \sqrt{\frac{\sum_1^n (M-O)^2}{n}}$$

$$\mathrm{MB} = \frac{1}{n}\sum_1^n (M-O)$$

$$\mathrm{IOA} = 1-\frac{\sum_1^n (M-O)^2}{\sum_1^n (|M-\bar{O}|+|O-\bar{O}|)^2}$$

M and O represent modeled and observed outputs, respectively.

Observation periods were varied by site: In the Olympic Park station, the data were produced from May 17 to June 12, while in the Taehwa Mountain, the observations were made from May 5 to June 12 (see top panel on the Figure 2). Although $ClNO_2$ was measured only at these two sites, the observed levels are comparable to those reported in the previous studies (Mielke et al., 2011; Wang et al., 2017).

We have also added two more references for the KORUS-AQ campaign (Crawford et al., 2021; Jeong et al., 2023) (please refer to line 113)

Comment 2: In section 3.1.1, there is an emphasis to state that adding the three-species halogen chemistry helped in bringing the model results closer to observed (lines 340-342 for example), compared to EXP_{CMAQ}. But most of these changes (75% or so) are solely due to updating the chlorine scheme. Have you compared EXP_{CMAQ} against EXP_{Cl} and $EXP_{Cl\text{-}Br}$? I think the emphasis in this section should be changed to how updating the Cl mechanism by adding new reactions and changing the parameterization of N_2O_5, brings down nighttime ClNO2 levels, followed by the impact of the addition of the HOBR reaction.

Reply: We agree with your comment, and have conducted an additional comparison among EXP_{CMAQ}, EXP_{Cl}, and EXP_{Cl_Br}, as shown in the Figure R1.

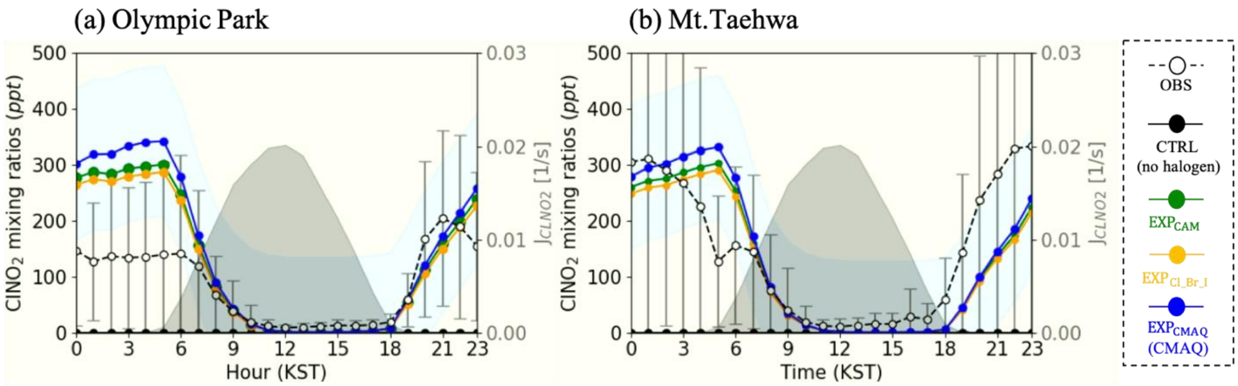

Figure R1. Diurnal variations in the mixing ratios of $ClNO_2$ (unit: ppt) at (a) Olympic Park and (b) Mt.Taehwa stations during the period of the KORUS-AQ campaign. Observed values are represented by open circles (error bars indicate the standard deviation). Colored lines with shaded areas show the hourly-averaged mixing ratios of $ClNO_2$ and the corresponding standard deviation from each simulation. The black shaded area indicates the variations in the photolysis rate of ClNO2 derived from the $EXP_{Cl\_Br\_I}$ simulation

In the Fig. R1, most of the changes in simulated $ClNO_2$ levels can be attributed to the updated chlorine chemistry (EXP_{Cl}). We have revised Section 3.1.1 to emphasize this point, more focusing on the impacts of the updated Cl chemistry, followed by the Br-related reactions (please, refer to lines 404-407).

Comment 3: In section 3.1.2, can you elaborate on the sensitivity test and how it was conducted? Were all reactions considered and these four reactions stand out or was there a reason to pick only these 4? Given the uncertainties in the partitioning of N_2O_5 onto chloride containing particles in the model being a big source for the change, have you tried testing any other parameterizations other than the one used?

Reply: To identify the key reactions, we conducted multiple sensitivity tests with variable mixing ratios of atmospheric halogen species and reaction rates. We then excluded the reactions the contributions of which to $ClNO_2$ productions were less than ~1%.

Given the uncertainties in N_2O_5 partitioning onto chloride-containing particles, we also tested three different parameterizations. Among them, the schemes selected in this study showed the best performances in reproducing observed $ClNO_2$ levels (refer to Table R1).

Table R1. Statistical analysis of $ClNO_2$ mixing ratios using different N_2O_5 parameterizations from Bertram and Thornton (2009), Davis et al. (2008), and this study.

(a) Olympic Park

	Bertram & Thornton (2009)	Davis et al. (2008)	This study
Mean Bias (ppt)	44.09	43.20	31.62
Root Mean Square (ppt)	200.98	196.24	179.4
Index of agreement	0.63	0.64	0.66
Simulated mean (ppt)	130.08	129.18	117.6

(b) Mt.Taehwa

	Bertram & Thornton (2009)	Davis et al. (2008)	This study
Mean Bias (ppt)	-22.38	-23.57	-31.4
Root Mean Square (ppt)	280.47	275.86	272.4
Index of agreement	0.57	0.57	0.58
Simulated mean (ppt)	136.98	135.79	128.0

Comment 4: Can you write more about the differences between EXP_{CAM} and either EXP_{CMAQ} or $EXP_{Cl-Br-I}$? The $ClNO_2$ is near-zero in EXP_{CAM}. Is this because of missing reactions in the 2014 version of CAM-Chem that was adopted and tested against here? There may have been updates and modifications to that scheme as well, so maybe a more recent version (if changed) might be useful for discussion.

Reply: As noted in the revised manuscript, EXP_{CAM} was originally designed to simulate coastal conditions, which can limit the capability to reproduce the levels of $ClNO_2$ over NOx-rich continental regions such as the Korean Peninsula. It is likely that this may explain the near-zero $ClNO_2$ concentrations simulated from EXP_{CAM}. We provided more detailed explanations in the revised manuscript regarding this point (please, refer to lines 341-347 in the revised manuscript).

Comment 5: I wonder if there can be some discussion on uncertainties in the simulations (could be in the supplementary), especially considering that some of the changes seem to be on the smaller side - such as changes in ozone (in terms of percentage changes). I appreciate that is because of the competing reactions that affect the formation and destruction of ozone. But are these changes significant?

Reply: We agree with your point. Incorporating the full halogen chemistries and processes into the CMAQ simulations may be very challenging due to several following uncertainties: (i) high spatio-temporal variability in halogen emissions, (ii) omissions of potential reactions, and (iii) limited availability and accuracy of observational data. We added these limitations in our revised manuscript (please, refer to lines 689-695).

Although the changes in O_3 appear to be small in South Korea due to the competing effects between halogen-induced production and destruction, it is still important to incorporate sophisticated halogen reactions in modeling simulations. Halogen chemistries not only affects ozone levels but also radical chemistry in the atmosphere, potentially enhancing the lifetime of greenhouse gases such as CH_4 (Li et al., 2022; A.Saiz-Lopez et al., 2023). This is the necessity to highlight the detailed halogen reactions in the atmospheric models.

Comment 6: Is the updated version of the model code and the results going to be available to the public? If so, can you give the location for that as well in addition to the CMAQ web page.

Reply: This study was conducted as a part of a national project to develop the Korean Air chemistry Modeling System (K_ACheMS). Model code is not publicly available at this moment, but it can be provided upon request.

[Minor Suggestions]

Comments 1: Line 83: Change examines to examine.
Reply: We revised it.

Comments 2: Line 274: CCHO should be CH3CHO.
Reply: We revised it.

Comments 3: Line 381: Maybe use "Future" instead of "Further".
Reply: Thank you for your correction. We changed it.

Comments 4: Line 578: I think "attempted to incorporate" can be modified because CMAQ modeling systems already exist with some halogen processes. Maybe being clearer that you added and updated three halogen species reactions in the CMAQ modeling system would be better.
Reply: We clarified this point in the revised manuscript. Please check out lines 230-233.

Comments 5: Figure 3b: Perhaps this is a rounding error, but the sum of the percentages in the pie chart add up to 100.1%.
Reply: We corrected this (please, see Fig. 3b).

Comments 6: Figure 3: In the caption, can you add that the grey regions are night-time?
Reply: We added it (please, see Fig. 3).

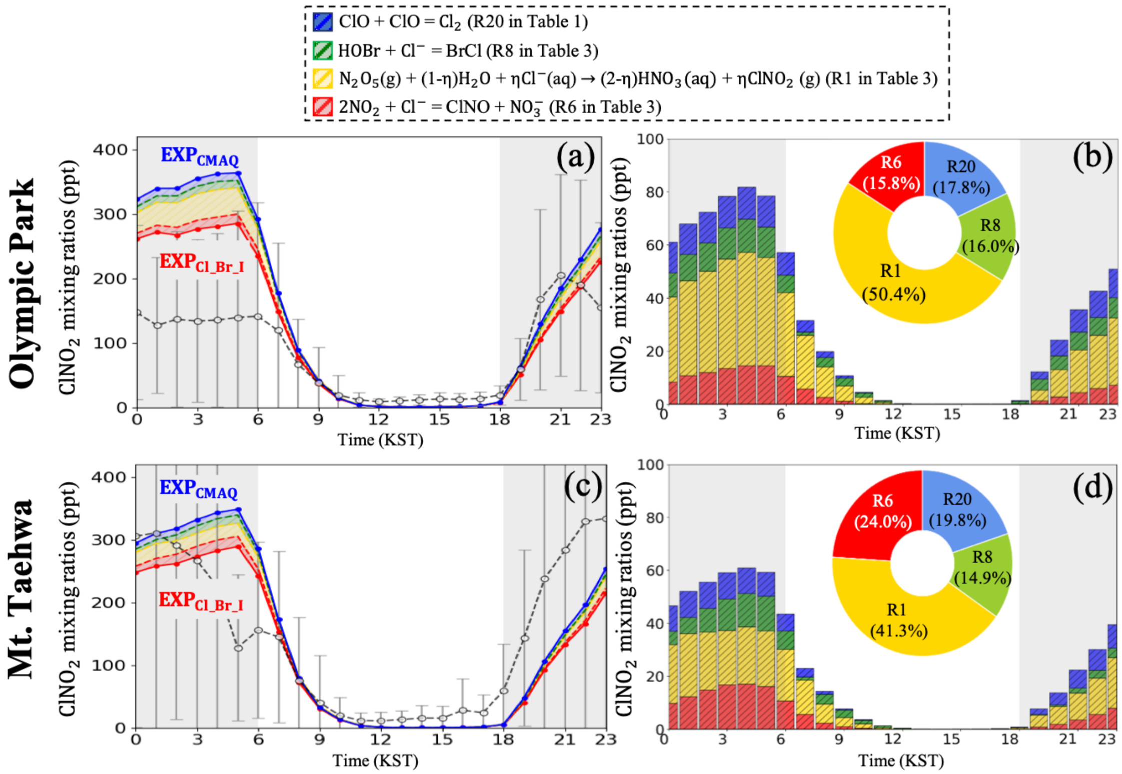

Figure 3. Contributions of halogen reactions to the mixing ratios of $ClNO_2$ in the EXP_{CMAQ} and $EXP_{Cl\_Br\_I}$ simulations at (a and b) Olympic Park and (c and d) Mt. Taehwa stations during the period of KORUS-AQ campaign. Stacked bars and pie charts show the contributions from four halogen reactions to the mixing ratios of $ClNO_2$. Grey-shaded areas represent nighttime (18:00-06:00 local standard time).

Comments 7 Figure 5: What do the DIFF's stand for? Why is it MAX for the top two and MIN for the bottom panel? Are the standard deviations and error bars for the observed?
Reply: The 'DIFF' values represent the difference in average concentrations between simulations during the analysis period. The 'MIN' and 'MAX' mean the minimum and maximum of these average differences. We though that these are a bit out of context. Thus, we removed it.

To further clarify the meaning of DIFF and to avoid any confusion regarding the standard deviation and error bars, we have updated the Figure caption (please, refer to Fig. 6).

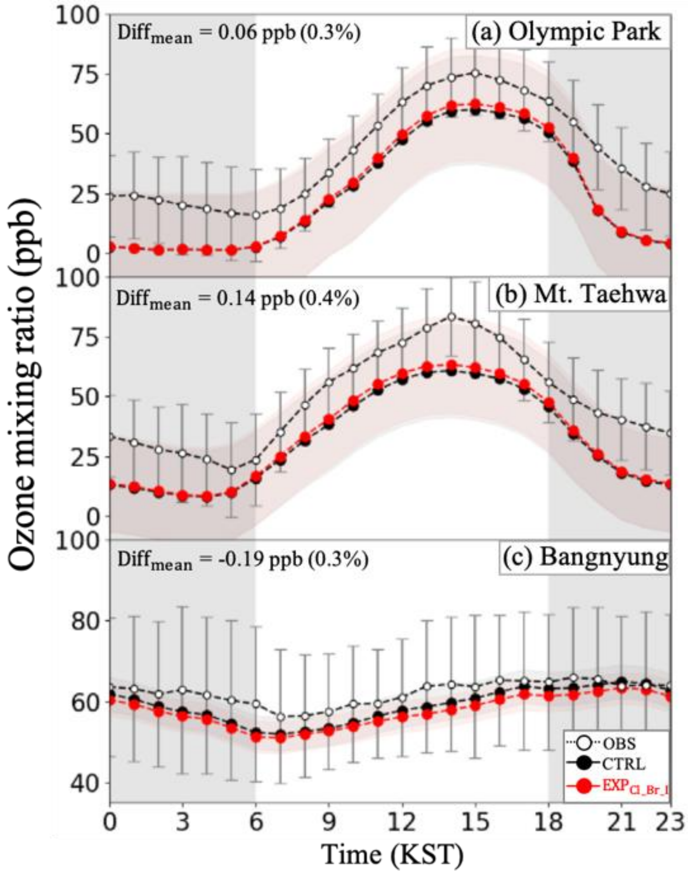

Figure 6. Diurnal variations in the mixing ratios of O_3 from CTRL (black circles) and $EXP_{Cl\_Br\_I}$ (red circles) simulations, together with observed mixing ratios of O_3 (OBS; white circles) at (a) Olympic Park, (b) Mt. Taehwa, and (c) Bangnyung stations during the period of the KORUS-AQ campaign. Error bars and shaded areas indicate the standard deviations of observed and modeled O_3, while the grey-shaded areas show the nighttime. $DIFF_{mean}$ represents the difference in the averaged mixing ratios of O_3 between $EXP_{Cl\_Br\_I}$ and CTRL simulations.

Comments 8: Figure 8: Can you add the mean values of changes within or in top of the panel each of the species & simulations? It would be nice to see what the changes are for each of these experiments within the figure itself. At least for the full halogen process panel.

Reply: We added them in revised Fig. 9.

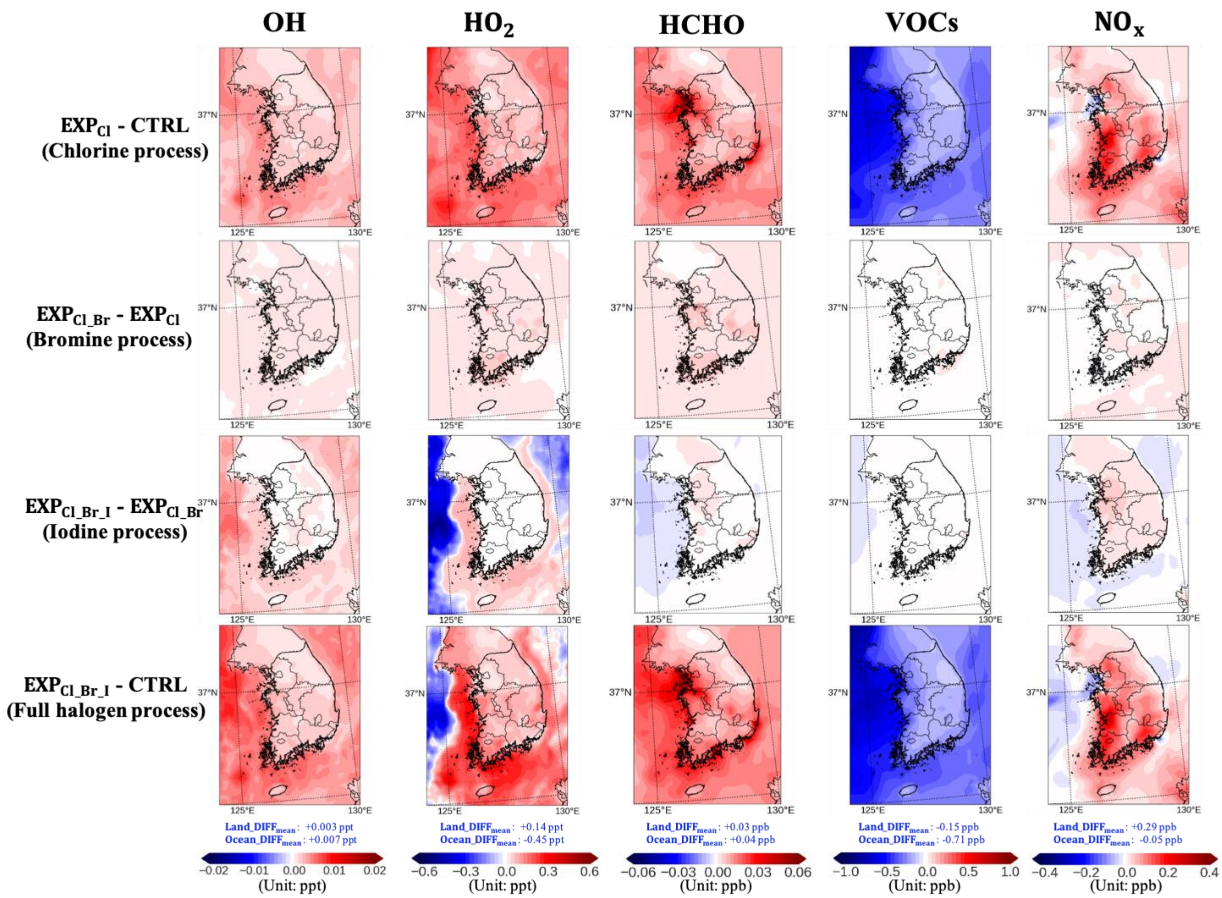

Figure 9. Summaries of the impacts of chlorine processes (EXP_{Cl} – CTRL), bromine processes (EXP_{Cl_Br} – EXP_{Cl}), iodine processes ($EXP_{Cl\_Br\_I}$ – EXP_{Cl_Br}), and full halogen processes ($EXP_{Cl\_Br\_I}$ – CTRL) on the mixing ratios of OH, HO_2, HCHO, VOCs, and NO_x, respectively, during the period of KORUS-AQ campaign. Also, $Land\_DIFF_{mean}$ and $Ocean\_DIFF_{mean}$ indicate the differences in the averaged mixing ratios of each species between $EXP_{Cl\_Br\_I}$ and CTRL simulations, over land and ocean, respectively.

Reference cited in this response:

Mielke, L. H., Furgeson, A., & Osthoff, H. D. (2011). Observation of ClNO2 in a mid-continental urban environment. *Environmental Science & Technology*, *45*(20), 8889-8896.

Wang, X., Wang, H., Xue, L., Wang, T., Wang, L., Gu, R., ... & Wang, W. (2017). Observations of N2O5 and ClNO2 at a polluted urban surface site in North China: High N2O5 uptake coefficients and low ClNO2 product yields. *Atmospheric environment*, *156*, 125-134.

Crawford, J. H., Ahn, J. Y., Al-Saadi, J., Chang, L., Emmons, L. K., Kim, J., ... & Kim, Y. P. (2021). *The Korea–United States Air Quality (KORUS-AQ) field study, Elem. Sci. Anth., 9, 00163*.

Jeong, D., Seco, R., Gu, D., Lee, Y., Nault, B. A., Knote, C. J., Mcgee, T., Sullivan, J. T., Jimenez, J. L., Campuzano-Jost, P., Blake, D. R., Sanchez, D., Guenther, A. B., Tanner, D., Huey, L. G., Long, R., Anderson, B. E., Hall, S. R., Ullmann, K., Shin, H., Herndon, S. C., Lee, Y., Kim, D., Ahn, J., and Kim, S.: Integration of airborne and ground observations of nitryl chloride in the Seoul metropolitan area and the implications on regional oxidation capacity during KORUS-AQ 2016, Atmos. Chem. Phys., 19, 12779–12795, https://doi.org/10.5194/acp-19-12779-2019, 2019.

Li, Q., Fernandez, R.P., Hossaini, R. *et al.* Reactive halogens increase the global methane lifetime and radiative forcing in the 21st century. *Nat Commun* **13**, 2768 (2022). https://doi.org/10.1038/s41467-022-30456-8

Saiz-Lopez, A., Fernandez, R.P., Li, Q. *et al.* Natural short-lived halogens exert an indirect cooling effect on climate. *Nature* **618**, 967–973 (2023). https://doi.org/10.1038/s41586-023-06119-z