

## Response to Reviewer #2

We would like to thank Reviewer #2 for the valuable comments especially those about the uncertainties in the model. It enables us to improve our study and the manuscript remarkably. In the following, we address the issues raised by the reviewer point by point.

### Major Comments:

**Q2.1:** The main criticism of the manuscript is that it does not convince the reader about the applicability of the model for reproducing ozone depletion considering the specific tuning of the model to get the ozone right. This tuning suggests that the emissions and chemistry are not correctly described in the model even if it gets the meteorology right. Considering this, I cannot recommend that this paper be published in its current form. I would prefer to see a more detailed section highlighting the uncertainties, with some quantification of the uncertainties using sensitivity analysis. The value of the paper would come from understanding what needs to be improved rather from the using of tuning to reproduce two ODEs. From the results, the model does well at getting the meteorology correct, so the issue should be with the emissions and chemistry. How would this paper help in understanding which is the main issue and what needs to be improved?

**A2.1:** First of all, we would like to express our sincere thanks to the reviewer for this comment. It is true that our model needs some modifications especially in boundary conditions in order to capture some of the ODEs. In our opinion, these modifications in models are inevitable due to the complexity of ODEs and the insufficient capability of existing models. To our knowledge, the ODEs are associated with many complex processes such as the boundary layer physics, halogen chemistry and kinetics of heterogeneous reactions. Simulating all these processes precisely is a big challenge to all the existing models especially the 3-D models. For instance, simulating the stable boundary layer, which is normally observed during ODEs, is difficult for models. Moreover, there exists a large uncertainty in halogen emissions used in models. In addition, the global models, which

provide results for the boundary conditions of meso-scale models, normally do not consider the influence of the halogen chemistry. At present, the widely used meso-scale models include WRF-Chem, CMAQ and CMAx, in which reasonable modifications and assumptions in the model are all required to simulate ODEs.

In our study, we tried to simulate ODEs using CMAQ, in which the halogen chemistry is originally included in the chemical mechanism. The advantage of CMAQ is that it can quantitatively estimate the contribution of each physical or chemical process to the variations of chemical species such as ozone using the process analysis method. Thus, ideally, we should be able to not only reproduce the ODEs, but also quantify the contribution of each process to the ODE. However, due to constraints in computing resources, we can only run the simulation using the current computational domain and the time interval.

The reviewer is also correct saying that the deviations between simulations and observations may come from emissions and chemistry. In our model, the release of bromine was included by implementing the heterogeneous reaction  $\text{HOBr} + \text{ASEACAT} \rightarrow \text{Br}_2 + \text{H}_2\text{O} + \text{ASEACAT}$ , but the rate of this heterogeneous reaction in our model is uncertain. Moreover, the iodine chemistry was also not considered in the mechanism of the model. Furthermore, we think the boundary condition provided by the global model is also a major factor for the deviations because the halogen chemistry and the ozone depletion is normally not considered in global models. Thus, according to the suggestion of the reviewer, during the revision process, we performed many sensitivity tests by altering the rate of the heterogeneous reaction and changing the implemented boundary conditions. These new results were included in the revised manuscript as a new section (**Section 3.4 Sensitivity tests**). These results are also presented in the answer to the next question **A2.2** in this rebuttal.

For the implementation of the iodine chemistry, currently we are unable to add it into the chemical mechanism of the model. In the future, we will try to use a mechanism (CB6r3m) with more comprehensive halogen chemistry including the iodine chemistry, which is

included in CMAQ version 5.3. We also mentioned it in the last section of the revised manuscript, please see [lines 500-505](#).

**Q2.2:** The increase in  $k_{R3}$  by one order of magnitude is justified by saying that it helps explain the ODE – no comparison with bromine observations is offered. This begs the question, is the model getting the ODE right for the wrong reasons? No uncertainty evaluation has been done to find the sensitivity of the model to  $k_{R3}$  or if any other factors can help in explaining the ODEs. The authors mention that ‘ozone and other species in the computational domain can be greatly affected by the implemented boundary conditions’ – so how much confidence do they have in the model simulations and which is the main driver of the uncertainty?

**A2.2:** Thanks a lot for the comment. As we mentioned in the answer **A2.1** above, according to the suggestion of the reviewer, we performed many sensitivities tests on the reaction rate  $k_{R3}$  and the implemented boundary condition to illustrate the uncertainties of the model. Some of the results are presented below.

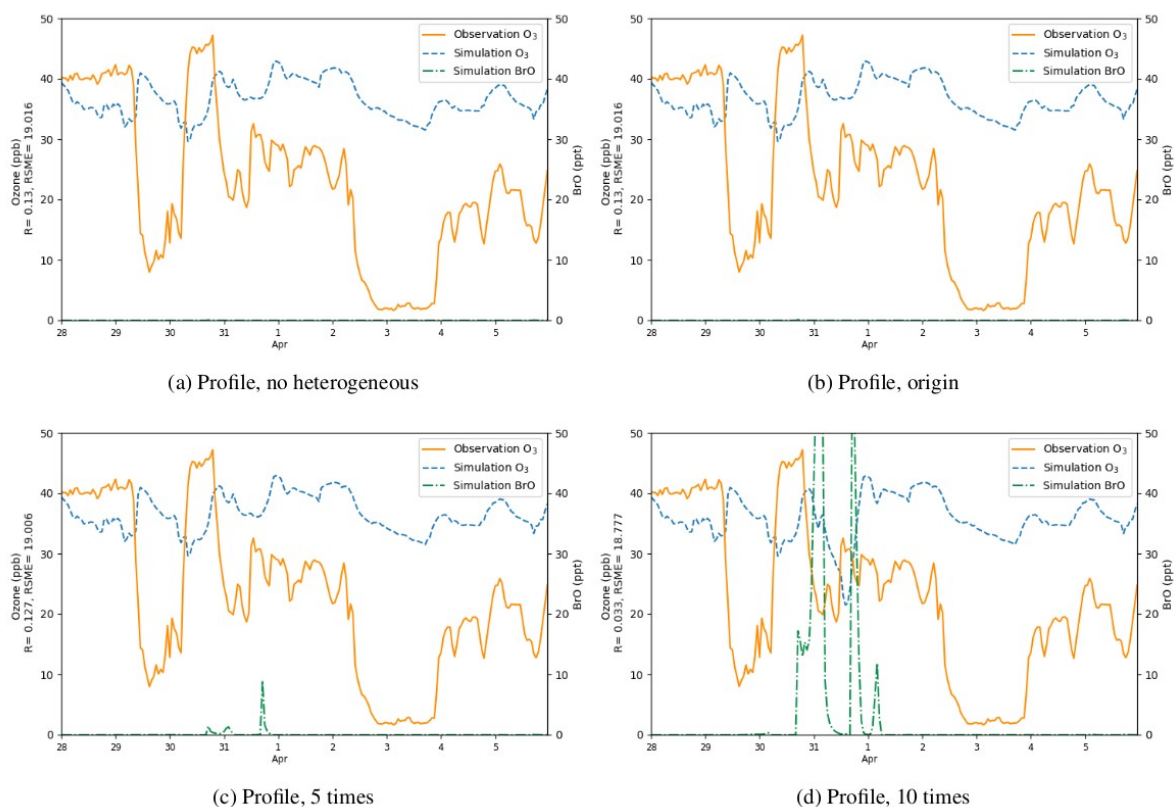


Figure 1 Surface ozone (ppb) and BrO (ppt) at Barrow from 28 March to 5 April, 2019, obtained from CMAQ simulations using different heterogeneous reaction rates and the default boundary condition, i.e., a static ozone profile. The correlation coefficient R and the root-mean-square error RMSE were also presented in the vertical axis.

Results of the sensitivity tests in which the heterogeneous reaction rate was altered are shown in Fig. 1 of this rebuttal. In this series of sensitivity tests, we used the default boundary condition (BC) of ozone in CMAQ. This default BC in CMAQ is generated by a static profile, which represents annual average concentrations over the Pacific for the year 2016. This BC reflects conditions in a remote marine environment. From Fig. 1(a), we found that with the default BC but without the heterogeneous reaction for the bromine explosion, the simulated ozone did not show any obvious depletion and the level of BrO was close to zero. Then we added the heterogeneous reaction  $\text{HOBr} + \text{ASEACAT} \rightarrow \text{Br}_2 + \text{H}_2\text{O} + \text{ASEACAT}$  responsible for the bromine explosion into the mechanism, with the reaction rate suggested by Mellberg (2014) (Fig. 1b), but found the changes in ozone and BrO negligible. Thus, we

continued to enlarge the heterogeneous reaction rate. In Fig. 12(c), the reaction rate was 5 times larger than that suggested by Mellberg (2014). In this simulation, we found the BrO level at Barrow elevated, to a value range of 0-10 ppt. However, ozone did not show any remarkable change and the simulated value was still higher than the observations. In Fig. 1(d), we enlarged the heterogeneous reaction rate to a value that is 10 times of that suggested by Mellberg (2014), and we found the ozone during the time period of ODE1 (i.e., 31 March) decreasing to a level similar to observations. Moreover, BrO was also substantially elevated, with a peak higher than 50 ppt. However, ozone concentrations in other time periods were still not significantly influenced by the change of the reaction rate.

Table 1 Values of the Pearson correlation coefficient (R) and the root-mean-square error (RMSE, unit: ppb) for the simulated surface ozone at Barrow under different conditions (the heterogeneous reaction rate and boundary conditions).

Rate \ BC	Default (R, RMSE)	CAM-Chem (R, RMSE)	CAM-Chem (reduced) (R, RMSE)	CAM-Chem (reduced & modified) (R, RMSE)
0	0.130, 19.015			0.803, 8.339
1	0.130, 19.016			0.803, 8.339
5	0.127, 19.006			0.803, 8.339
10	0.033, 18.777	-0.398, 30.185	0.653, 10.223	0.802, 8.347

The statistical parameters for the simulated surface ozone at Barrow using different heterogeneous reaction rates are listed in Tab. 1 in this rebuttal. We can see that when the default static BC was used, the correlation coefficients were all close to 0.1. Furthermore, the RMSEs were also large. We also performed a simulation using a reaction rate that is 15 times of the rate proposed by Mellberg (2014), and the simulation results even show a negative correlation with the observations. Thus, from this series of sensitivity tests, we concluded that the heterogeneous reaction is only able to affect the simulated ozone and BrO during the time period of ODE1 (i.e., 31 March). For other time periods, other factors such as the implemented boundary conditions (BCs) might play important roles.

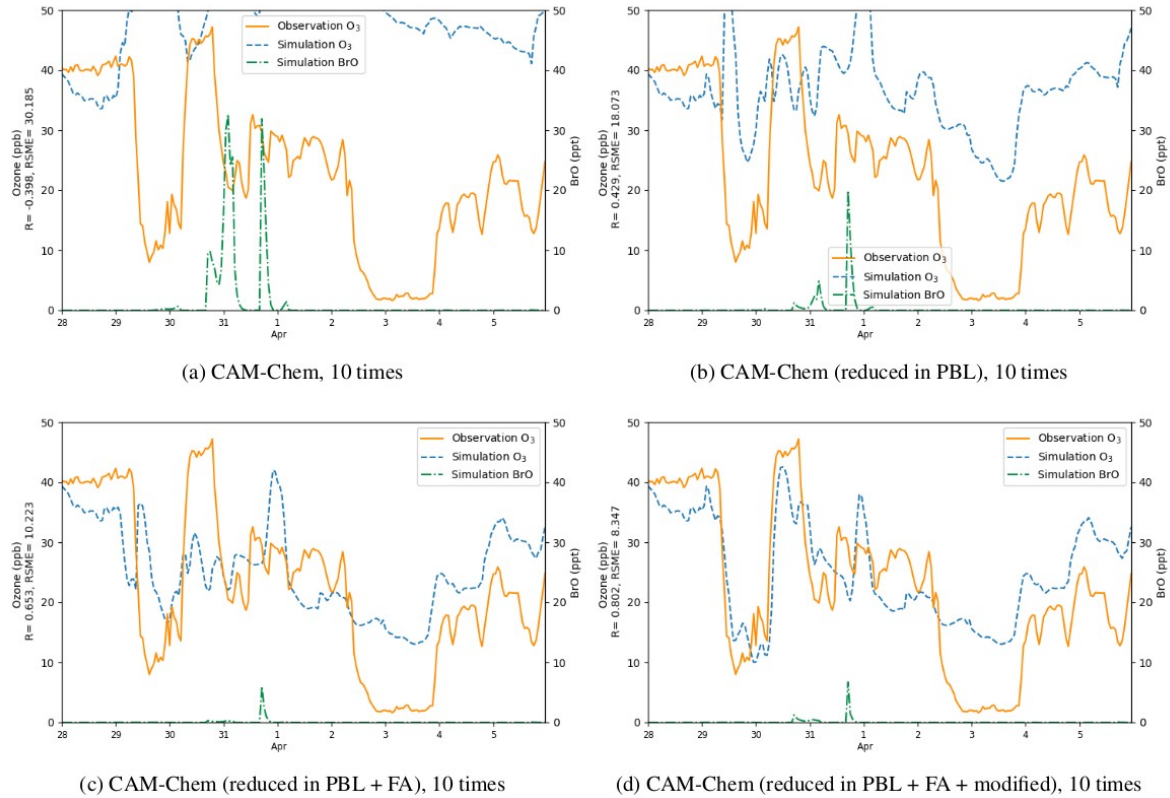


Figure 2 Surface ozone (ppb) obtained from simulations and observations together with the simulated BrO at Barrow from 28 March to 5 April, 2019. The correlation coefficient  $R$  and the root-mean-square error RMSE were also presented in the vertical axis. Simulations were performed using different boundary conditions: (a) time-dependent boundary conditions adopted from the outputs of CAM-Chem, (b) outputs of CAM-Chem with a reduction of ozone in the PBL, (c) outputs of CAM-Chem with a reduction of ozone in the PBL and the free atmosphere, (d) outputs of CAM-Chem with a reduction of ozone in the PBL and the free atmosphere as well as a modification of ozone over the Chukotka Peninsula.

Then we tested different boundary conditions in simulations (Fig. 2 in this rebuttal). We first replaced the default BC with the outputs of the CAM-Chem model (Fig. 2a), but found the simulated ozone significantly higher than the observed values. As shown in Tab. 1, the correlation coefficient for this simulation is negative and the RMSE reaches 30.185 ppb. The reason for this large deviation might be the BC of ozone adopted from the CAM-Chem model does not take the influence of the bromine chemistry into account. Thus, we modified the outputs of the CAM-Chem model based on observations (Bottenheim and Chan, 2006),

by reducing the ozone in the PBL in the BC according to types of the underlying surfaces. Figure 2(b) shows that after this modification, compared with the previous simulation, the simulated ozone is lower during the whole time period, and the RMSE also decreases. It means that the BC of the model can substantially affect the simulation of ODEs at Barrow under the investigation of this study. However, the difference between the simulation results and the observations is still moderate. Then we discovered that the ODEs cannot only be affected by the air in the PBL, but also the air in the free atmosphere. Moreover, ozone in the free atmosphere can also be influenced by the bromine explosion (Bottenheim and Chan, 2006). Thus, we continued to reduce the free atmospheric ozone in the BC of the model (see Fig. 2c). It was found that the simulated ozone becomes lower than the previous simulation, denoting that the air transported from the free atmosphere also contributed to the ozone decline observed at Barrow. At last, we found that the ozone value over the Chukotka Peninsula in the BC of the model may exert a significant impact on the ODE on March 29. Therefore, we modified the ozone over the Chukotka Peninsula in the BC of the model (see Fig. 2d). As a result, the simulation of the ODE on March 29 becomes more consistent with the observations, especially the termination of this ODE. Thus, we suggested that this ODE at Barrow is highly associated with the air transported from the Chukotka Peninsula.

Bottenheim, J.W. and Chan, E.: A trajectory study into the origin of spring time Arctic boundary layer ozone depletion, *Journal of Geophysical Research: Atmospheres*, 111, <https://doi.org/10.1029/2006JD007055>, 2006.

Mellberg, J.: Final Report Ozone Depletion by Bromine and Iodine over the Gulf of Mexico, Tech. rep., Texas Commission on Environmental Quality, 2014.

**Q2.3:** Boundary conditions for ozone – the authors have applied their boundary conditions for ozone using arbitrary values without further explanation. They have changed the CAM-Chem outputs to ‘For the ozone in the boundary layer if it is on the surface of sea ice, ozone was set to 3 ppbv; if it is over the sea, ozone was set to 10 ppbv; if it is at a coastal area,

ozone was set to 15 ppbv. Furthermore, because the free atmospheric ozone can also be remarkably affected by the bromine explosion and the ODEs, ozone in the free troposphere in the implemented boundary condition was also reduced to half of the original value to consider the influence of the bromine explosion', mentioning that further information is in the code availability section. However, this section just lists the input data with no explanation for why these values are used and what observations they base these values on. One gets the impression that the model has been tuned to simulate the observed ozone depletion, hence quantification of the effect of chemistry and dynamics is inherently biased.

**A2.3:** Thanks. We modified our boundary conditions for ozone according to the study of Bottenheim and Chan (2006). In their study, air with low O<sub>3</sub> mole fractions was found to have normally passed over the Arctic Ocean. Moreover, Bottenheim and Chan found that over the Beaufort Sea and the Chukchi Sea, where the sea ice is frequently formed, the ozone value in the lower troposphere is in a range of 0-5.2 ppb. Thus, in the boundary conditions of the model, when the air is in the boundary layer and over the sea ice, we set the ozone value to 3 ppb. Meanwhile, in the study of Bottenheim and Chan (2006), over the open sea and coastal area, the range of ozone was found to be 5.2-13.85 ppb and 5.2-24.45 ppb, respectively. Thus, in our model, if the air is over the sea, the boundary layer ozone was set to 10 ppb; and if the air is at a coastal area, the boundary layer ozone was set to 15 ppb. In addition, in the study of Bottenheim and Chan (2006), they also suggested that the free tropospheric air can be remarkably affected by the bromine explosion, and ODEs can also be influenced by the air transported from the free troposphere. Thus, in the boundary conditions of the model, ozone in the free troposphere was also reduced to consider the influence of the bromine explosion.

We have added more explanations about the ozone values set in the model. Please see [lines 139-150](#) in the revised manuscript. A series of sensitivity tests on the implemented boundary conditions were also performed as mentioned above in previous answers. Please see [Section 3.4 Sensitivity tests](#) in the revised manuscript.



Bottenheim, J.W. and Chan, E.: A trajectory study into the origin of spring time Arctic boundary layer ozone depletion, *Journal of Geophysical Research: Atmospheres*, 111, <https://doi.org/10.1029/2006JD007055>, 2006.

**Q2.4:** This issue is also acknowledged by the authors on lines 190-193 – ‘It can be seen that without this adjustment, the simulated ozone on March 29th would be largely different from the observations. Hence, the skill of the model to simulate ozone is doubtful.

**A2.4:** Thanks. As we mentioned above, in our study, simulations of ODEs can be greatly influenced by many factors such as the implemented boundary conditions. To our knowledge, the simulation results can be improved in two ways. One is to use a larger computational domain so that the influence of the boundary conditions might become minor. However, running with a larger domain requires more computing resources, which is affordable for us at present. The other way is to use a more precise boundary condition. That is the reason we adopted the outputs of CAM-Chem and tried to modify the boundary conditions according to observations in the present study. The uncertainties in simulation results caused by using different boundary conditions were presented and discussed in the revised manuscript. Please see [lines 407-423](#) in Section 3.4. We also added more discussions on limitations of the model in the revised manuscript. Please see [lines 505-507](#).

**Q2.5:** Maximum concentrations of BrO, peaking at above 100 ppt are much higher than reported anywhere in the Arctic. This suggests that the model is not able to simulate the bromine well and/or suffers from the lack of other sinks for ozone. Recently it has been shown that iodine also plays an important role in the magnitude of ODEs in the Arctic (Benavent et al., 2022). The overestimation of BrO could be a result of missing chemistry.

**A2.5:** Yes, the lack of iodine chemistry in our model is one of possible reasons which may lead to the overestimation of BrO in our study. Thus, in the future, we will use a more comprehensive mechanism (CB6r3m\_ae7\_kmtbr), which has been implemented in CMAQ version 5.3 and includes the iodine chemistry. The reason we did not use this version of

CMAQ in this study is that running CMAQ 5.3+ requires a special OCEAN file, which can only be generated by EPA to describe the surf zone and DMS emissions and currently we are still lack of this file.

We added more contents discussing the shortcomings of the model and our future work. Please see [lines 500-505](#).

**Q2.6:** The authors could also compare the tropospheric bromine column from the model to satellite observations. This would offer some validation of bromine chemistry.

**A2.6:** Thanks a lot for the comment. We fully agree with the reviewer that the satellite observations of BrO columns can be used to validate our simulation results. Unfortunately, we did not have any experience in processing satellite data before. However, in order to address this issue raised by the reviewer, during this revision process, we did our best to find corresponding satellite data from GOME-2b and processed them for the comparison (see Fig. 3 in this rebuttal).

However, we can only find a qualitative agreement between the simulated BrO and the observations. For example, in simulations and observations, regions with high BrO column density were both found to the northwest of Barrow on 30 March (see Fig. 3 in this rebuttal). Besides, in simulations, the maximum of BrO was found to be approximately 2000 nmol/m<sup>2</sup>, which is similar to the peak value in satellite observations. For a better comparison, improvements of the model such as adding the iodine chemistry and more heterogeneous reactions need to be made, which is attributed to a future work.

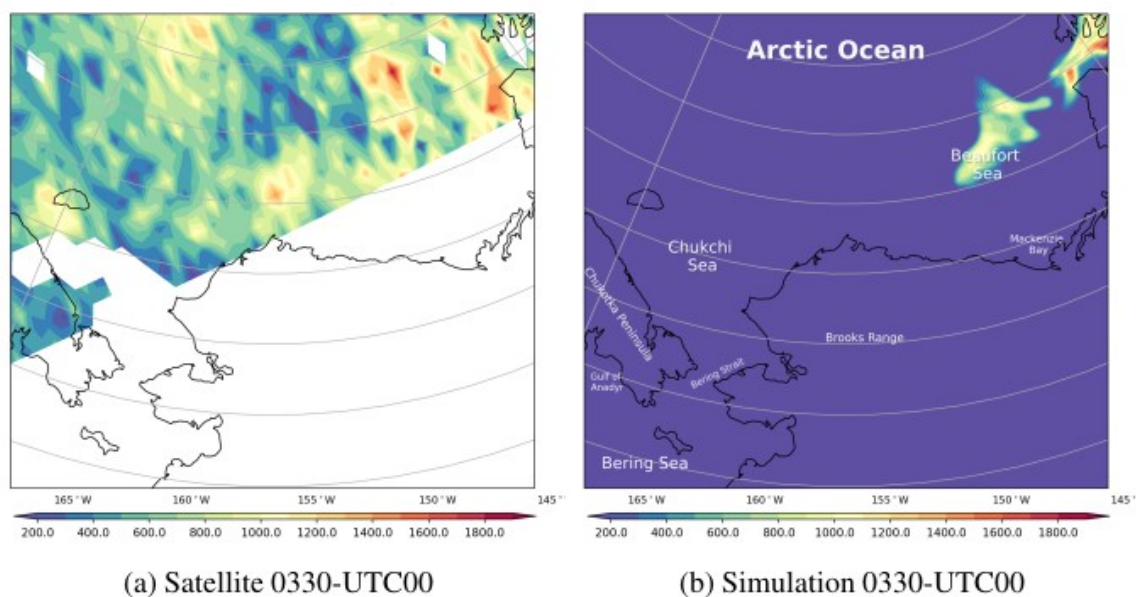


Figure 3 The tropospheric BrO column density (unit:  $\text{nmol}\cdot\text{m}^{-2}$ ) obtained in satellite observations and simulations at 00 UTC on 30 March 2019.

The comparison of BrO between the simulation results and the satellite observations was included and discussed in [lines 185-193](#) and [lines 244-249](#) in the revised manuscript. Thanks again for the comment which indeed improves our research and the manuscript.

**Q2.7:** Considering that the process analysis would be biased by the above assumptions. How valid are the numbers in figure 12 and what is the uncertainty in the ozone loss numbers? The paper would benefit from a detailed discussion on the uncertainties in the model for future improvement considering the large sensitivity of the model to the boundary conditions, initial ozone concentrations, and uncertainties in the assumptions for the emissions.

**A2.7:** Thanks for the comments. It can be seen from Fig. 1 and Fig. 2 in this rebuttal that the simulation results vary a lot under different assumptions and conditions. After performing many sensitivity tests, we found the simulations with the current setup the most accurate one among these tests. We then performed the process analysis based on this simulation. The advantage of PA module is that it can calculate the contribution of each process without

performing massive sensitivity tests. Thus, in our opinion, it might not be a good idea to perform sensitivity tests on the results of the process analysis. Of course we will try to improve our simulation results and perform PA for the improved results in the future.

For the uncertainties in the simulation results under different conditions, they have been presented and discussed in [Section 3.4](#) which has been described in our previous answers. Thanks again for the comment.

**Minor comments:**

**Q2.8:** Line 16: ‘In the Arctic, due to the lack of human activities, the tropospheric ozone remains at background level’ – this statement is not strictly true since ozone concentrations in the Arctic have increased due to long-range transport. (Sharma et al., 2019)

**A2.8:** Thanks. We modified this sentence to “the long-range transport of anthropogenic emissions of ozone precursors from North America and East Asia generally increases the tropospheric ozone in the Arctic since the 1990s (Sharma et al., 2019)”. Please see [lines 22-24](#) in the revised manuscript.

**Q2.9:** Line 19 – define ppbv

**A2.9:** Thanks. We added the definition of ppb in [line 22](#) in the revised manuscript.

**Q2.10:** Line 19 – .... commonly called ozone depletion events.

**A2.10:** Modified.

**Q2.11:** The reaction cycle (I) needs to be stoichiometrically balanced.

**A2.11:** Done. Thanks.

**Q2.12:** Line 28 - the total amount of Br and BrO keeps constant – rephrase to say that the total amount of bromine stays constant. ‘bromine species play as catalysts’ is not correct, both the species are not catalysts but rather bromine is.

**A2.12:** Thank you very much. We rephrased it to “the total amount of bromine stays constant, which means the bromine plays as a catalyst for the ozone depletion” in the revised manuscript.

**Q2.13:** Line 43: major oxidant in the atmosphere shifts from ozone to – ozone is not the major oxidant, but OH is.

**A2.13:** Thanks. We rephrased this sentence to “the dominant oxidant in the atmosphere shifts from OH, the major product of ozone photolysis, to bromine species”.

**Q2.14:** Line 47: ... the internal relationship...

Line 57 - ... and a high BrO ...

Line 75 and 110: ...which considers the halogen chemistry.

Line 110: originally instrumented used/implemented in CMAQ

**A2.14:** All done. Thanks a lot.

**Q2.15:** Line 114: Please give the webpage as a citation or include the list of reactions in the supplementary text.

**A2.15:** We now give the webpage as a citation according to the advice of the reviewer. Please see **line 123** in the manuscript and **line 566** in Section “References” in the revised manuscript.

**Q2.16:** Line 125 - For the ozone in the boundary layer

**A2.16:** Modified. Thanks.

**Q2.17:** Line 150 – The authors used ppb and ppbv interchangeably – please use only one form.

**A2.17:** We currently use ppb and ppt throughout the manuscript. Thanks a lot.

**Q2.18:** The language throughout the paper needs to be improved for grammatical errors. Several sections are missing or using too many articles and/or singular words have been

used instead of plural words. My suggestion is that either the journal helps with the language editing, or the authors use one of the several available services to improve the writing.

**A2.18:** Thank you for your suggestion. We tried our best to improve the quality of the manuscript and made many corrections during the revision process. An English native speaker was also invited to revise the manuscript. Please see the places marked in red and blue in the revised manuscript. Furthermore, we will use the ACP journal's (Copernicus Publications) typesetting and language copy-editing services to improve the paper's quality. Thank you again for the advice.

**Q2.19:** Line 186: 'It enables us for the subsequent analysis' – please rephrase.

**A2.19:** This sentence has been removed in the revised manuscript. Thanks for the comment.

**Q2.20:** Line 187- '...possibly due to the uncertainty in boundary conditions'. The mismatch could also be due to poor simulation of bromine chemistry or errors in reaction rates assumed for  $kR3$ .

**A2.20:** Thanks for the comment. To clarify it, we performed several sensitivity experiments to illustrate the uncertainties in simulations caused by the heterogeneous reaction rate and the implemented boundary conditions. Please see **Sect. 3.4** in the revised manuscript.

**Q2.21:** Please include the loss of bromine to deposition in figure 13.

**A2.21:** Thanks for the advice. In the revised manuscript, we show the contribution of dry deposition in this figure (see **Fig. 15** in the revised manuscript).