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Re: acp-2021-876 (The impacts of marine-emitted halogens on OH radical in East Asia during summer).

Dear editors,

We are grateful to the editors and the reviewers for the comments and suggestions. We have added following major modifications to address the reviewer's comments:

(1) We add more discussion about iodine chemistry to clearly reveal the driving factor on the spatial impacts on  $P_{OH}$ . In this context, the interaction of anthropogenic emission and iodine chemistry is discussed.

(2) Add more discussion about the limitations in the context of guiding further development of chemical reactions in models and further observations.

Following is a point-by-point response to the reviewer's comments. Texts in *Italic Bold* are the reviewers' comments, and those in normal black are our responses. The blue texts are revised sentences in the revised manuscript. All the line numbers in blue are referred to the change tracking version. We hope that you and the referees will find the changes satisfactory and we are looking forward to hearing from you soon.

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## **Responds to the reviewers' comments**

### **Reviewer #1:**

#### **Major:**

*1. How would anthropogenic pollutants interact with marine halogens? The authors have cited a wide range of previous studies (e.g., Sherwen et al., Wang et al.,) but most of these studies focus on the global scale where halogen chemistry is largely driven by natural processes. In this work, the studied area is subject to major anthropogenic influence. This is a question of great interest that many global models are difficult to address because of the coarser resolution. I would suggest that the authors expand on this, which places this work in the context of previous studies and greatly advances our current understanding of reactive halogen chemistry.*

#### **Response:**

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Thank you very much for your great comment. In previous study, the dependence of the activation of SSA Cl on anthropogenic pollutants NO<sub>x</sub> have been widely discussed, so we do not discuss it again in this work. What we focus on is the anthropogenic NO<sub>x</sub> and VOC pollutant influence on the reactive halogen chemistry. We add new simulations increasing ozone level by enlarge of NO<sub>x</sub> and VOCs emissions in the Philippines, where show very special negative change of  $\Delta P_{OH}$ , to illustrate the impact of anthropogenic emission influence on the iodine-chemistry-induced  $\Delta P_{OH}$ . The added content can be referred to the [line 514-558](#) in the revised manuscript.

*2. Figure 2 shows some striking discrepancies, which are, again, very intriguing. Section 3.3 and 3.4 are able to identify several processes that are probably less important. However, these sections fail to offer a clear explanation on what exactly drives the spatial variability of iodine-induced OH production. I have a few detailed suggestions in the next section to improve the clarity. In addition, I would also suggest that the authors provide a few more maps showing the surface seawater iodide field, the modeled marine emissions of I<sub>2</sub> and HOI, the modeled ozone dry deposition velocities, as well as the modeled HOI and sea salt aerosols in the surface air. Perhaps these can shed insights into the spatial variability of iodine-induced OH production in this region.*

**Response:**

Thank you very much for your great comment. We agree that driving factor for the contrast pattern of  $P_{OH}$  change, especially the negative change of  $P_{OH}$  in the Philippines Sea, is worthy to be explained further. We add spatial maps as suggested and further discussions to explain the discrepancies in the revised manuscript ([Line 481-514](#)).

**Specific comments:**

*1. Line 15: Please clarify how monthly OH production ( $P_{OH}$ ) is calculated. Does this involve nighttime signals?*

**Response:**

Yes, it is the average of 24×31 hourly  $P_{OH}$ . This is in line with previous global studies where only global mean OH is discussed (e.g., Sherwen et al. 2016a; Stone et al. 2018). Daytime average will be explicitly mentioned if it is the case.

*2. Line 33: This is a vague description. HO<sub>2</sub> -> OH is not always a net source of OH, since a major fraction of HO<sub>2</sub> is actually produced from OH. Please rewrite this sentence: either tease out the primary fraction of HO<sub>2</sub> (e.g., from formaldehyde) or discuss the sum of OH and HO<sub>2</sub>. After all the interconversion between OH and HO<sub>2</sub> is fast.*

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**Response:**

Thanks for the suggestion. We modify the manuscript as follows:

When there is abundant NO, as typically in the polluted continental atmosphere, peroxy radicals (RO<sub>2</sub>, and HO<sub>2</sub>) will be formed by the oxidation of hydrocarbons by OH, and will form OH again in the reaction with NO. This HO<sub>x</sub> (=OH+HO<sub>2</sub>) cycling maintain a high OH concentration that cannot be achieved by primary sources alone. (Line 48-51)

***3. Line 37: ... under low-NO<sub>x</sub> condition. Also please clarify what exactly is “low-NO<sub>x</sub> condition”. Is this referring to the condition when RO<sub>2</sub> fate is dictated by non-NO<sub>x</sub> pathways? If this is the case, often the NO<sub>x</sub> threshold can be very low.***

**Response:**

Yes, it is. Low-NO<sub>x</sub> condition is actually the very low NO<sub>x</sub> threshold. To avoid misleading, we modify the manuscript as follows:

Due to the complexity of the HO<sub>x</sub> chemistry, the sources and sinks of OH are not fully understood. For example, recent studies showed that when NO<sub>x</sub> concentration is very low there may be missing sources of OH. (Fittschen et al. 2019; Fuchs et al. 2013; Hofzumahaus et al. 2009; Lelieveld et al. 2008; Lu et al. 2019; Rohrer et al. 2014; Stone et al. 2012; Tan et al. 2019; Whalley et al. 2021). Besides, HO<sub>x</sub> chemistry can interact with other oxidizers in the atmosphere in specific circumstances. (Line 51-59)

***4. Line 40-43: The end of this paragraph is confusing and unclear how this is relevant for this manuscript.***

**Response:**

Thanks. It has been removed from the revised manuscript. Please see the response to comment #3 above.

***5. Line 46: ... under high NO<sub>x</sub> condition.***

**Response:**

Thanks. It has been removed from the revised MS. Please see the response to comment #3 above.

***6. Line 50: What is “long-term species”? I assume what the authors meant to say is “long-lived” since ozone lifetime is longer than, say, HO<sub>x</sub> radicals? If this is the case, this is clearly not true since ozone is not always constrained in box models. For instance, there are numerous studies focusing on halogen-induced ozone destruction in the Arctic and the combined effects on HO<sub>x</sub> and they use box model with ozone unconstrained.***

**Response:**

Thank you. Yes, we mean “long-lived”. We agree that ozone can be unconstrained

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in box models. In the Arctic, the focus is usually the ozone depletion events and ozone is indeed unconstrained. But many related studies do constrain O<sub>3</sub>.

We modify the sentence from “In box-model studies, long-term species such as O<sub>3</sub> are usually observation-constrained and cannot reflect the influence of halogens, probably resulting the difference between box models and CTMs (Stone et al. 2018).” to “In a box model, when the long-lived species such as O<sub>3</sub> are observation-constrained, it cannot reflect the complete influence of halogens, which probably result in the different results between box models and CTMs (Stone et al. 2018).” (Line 88-91)

**7. Line 45: “One relevant reaction is that XO (X=Cl, Br, and I) transform HO<sub>2</sub> to OH...” This is very confusing as written since this is not a one-step process: HOX is produced first, which may undergo photolysis and produce OH but HOX can also undergo heterogeneous uptake on aerosols (a major driver of halogen cycling).**

**Response:**

We agree that HOX may undergo heterogeneous uptake and activate particulate halogens but the rate of HOX uptake is much slower than the photolysis of HOX and almost all HOX would be photolyzed to form OH; therefore, the main result of XO+HO<sub>2</sub> is to transform HO<sub>2</sub> to OH, which has been adopted by many authors to explain the HOx cycle in the presence of XO. For example, (Saiz-Lopez and von Glasow 2012) stated that “In the presence of reactive halogens, the HOx balance is shifted towards OH.” To make it clearer, we rephrase the sentence from “XO (X=Cl, Br, and I) transform HO<sub>2</sub> to OH, as NO does in the high-NOx condition.” to “XO (X=Cl, Br, and I) shifts the HOx balance towards OH (Saiz-Lopez and von Glasow 2012).” (Line 65-66)

**8. Line 54: “... but it is not very clear which process will dominate” Respectfully, I disagree. Perhaps this is not explicitly spelled out in some studies, but the final model outcome speaks for itself. For instance, Wang et al., (2021) showed that the net effect of halogen chemistry on global tropospheric HOx is that both OH and HO<sub>2</sub> are reduced by 3-4%. This is buffered by many other processes but the primary driver is a global ~10% decrease in HOx production from ozone. This is qualitatively consistent with previous studies.**

**Response:**

We agree that the sentence is somewhat misleading, and we delete the sentence “but it is not very clear which process will dominate” and modify it as follows:

Even though we know all the important pathways, due to their opposite impacts on OH, we need further to understand the controlling processes of these pathways in order to better explain the trend of halogen-induced ΔOH in a specific circumstance. (Line 99-101)

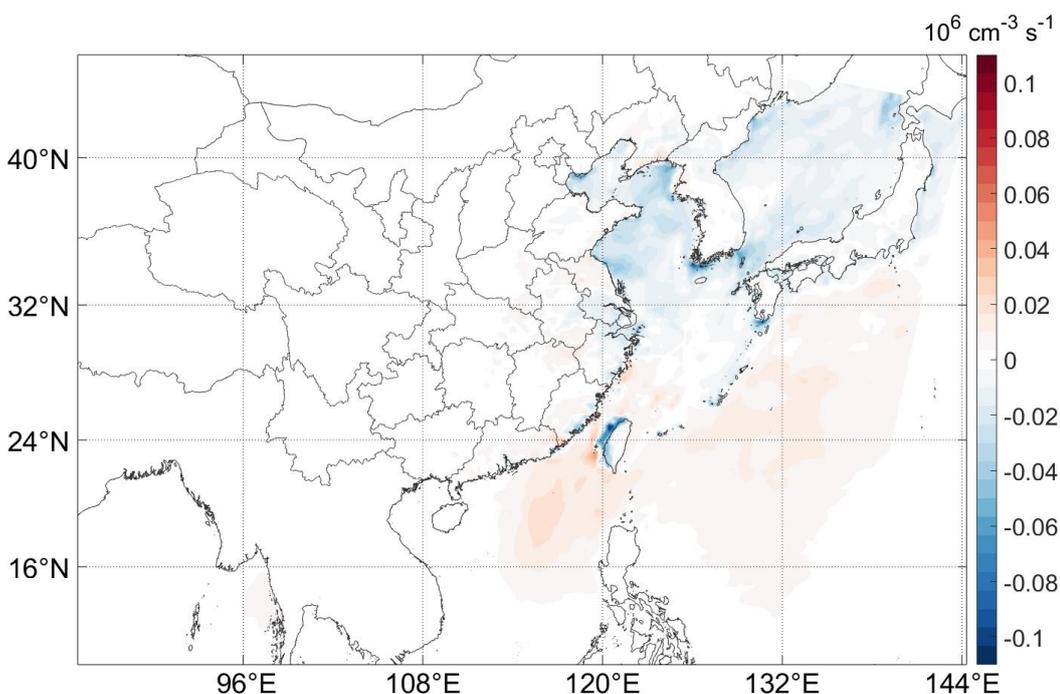
**9. Line 56-57: “For example, the conversion of HO<sub>2</sub> to OH enhanced by XO would consume HO<sub>2</sub>, which in turn should decrease the conversion through HO<sub>2</sub>+NO.**

*Previous CTM studies generally did not consider such an impact” I am confused. These two are competing processes with the same end goal, which is to convert HO2 to OH. As long as these relevant mechanisms are included in the model, the impact will be considered.*

**Response:**

Sorry for the confusing. The case is that all the relevant reactions are included in the model in previous study. They could be considered, but not yet been considered in the result explanation. We have deleted this sentence in the revised MS.

These two (HO2+XO and HO2 +NO) are processes with the same end. Our point is that HO2+NO and HO2+XO have different efficacy in converting HO2 and are differently influenced by the environment. With the competition of XO with NO, the conversion of HO2 to OH may be changed. That is why HO2 may not be converted more to OH by Cl and Br (and only I enhance the conversion of HO2 to OH significantly) as shown by the negative change of  $P_{OH\_HO2} + P_{OH\_HOX}$  in Fig. R1.



**Fig. R1** (Fig. S4b). Change of  $P_{OH\_HO2} + P_{OH\_HOX}$  caused by SSA Br chemistry (=case with SSA Br emission minus case without).

**10. Line 58-59: I failed to follow how exactly halogen chemistry can affect the photolysis of HONO and H2O2, ozonolysis of some alkene, ... Please clarify.**

**Response:**

Halogen chemistry has very complicated influence on HOx chemistry because there are lots of chemical feedbacks. HONO, for example, is primarily a product of heterogeneous reactions in CMAQ, which will consume NO2. As NOx is

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complicated influenced by halogen chemistry, the potential impacts on HONO cannot be excluded when we want to thoroughly quantify the impacts of halogen chemistry on HOx chemistry. We tracked all OH sources change under the impact of halogens. These three are chosen for illustrations. Of course, Fig. 2 just prove the unimportance of the halogens' impacts on these OH sources, but this is a result, not a premise.

**11. Line 63: “However, previous studies did not analyze the pathways...” Again I disagree with this statement. Globally, iodine chemistry alone may have largely compensating effect on OH (e.g., Sherwen et al., 2016) but the relative abundance of reactive iodine species and the impacts of iodine chemistry on the global tropospheric OH levels in the context of chlorine and bromine chemistry is shown in Wang et al. (2021): globally, the effect of halogen chemistry (including iodine) on OH, is a net reduction. The relative importance of iodine chemistry on the global scale thus can be inferred.**

**Response:**

We revise the sentence. Please see comment #8 above.

**12. Line 65-66: This is very vague as written. Do the authors refer to the reactive halogens (e.g., I<sub>2</sub>/HOI), debromination from sea salt, or the very short-lived substances (VSLS)? Please clarify. But generally this is a valid point, and more recent estimates certainly benefit from more comprehensive observations, thus yielding narrower ranges compared to earlier studies. Either way, a few representative citations are warranted. I'll list a few more recent studies for each broad topic for the author's consideration: Iodide-driven I<sub>2</sub>/HOI emission and ozone deposition (Carpenter et al., 2021; Chance et al., 2019; Inamdar et al., 2020; Karagodin-Doyennel et al., 2021; Pound et al., 2020; Sherwen et al., 2019; Wang et al., 2021); sea salt debromination (Zhu et al., 2019); VSLS (Lennartz et al., 2015; Ordóñez et al., 2012; Wang et al., 2019; Ziska et al., 2013).**

**Response:**

Thanks for your comment. Yes, it is. We revise the sentence as follows:

Moreover, since current estimations of marine halogen emissions, including SSA Cl and Br ions (and their activations), inorganic iodine (I<sub>2</sub> and HOI), and very short-lived halocarbons, have large uncertainties (Carpenter et al., 2021; Ordóñez et al., 2012; Ziska et al., 2013; Inamdar et al., 2020; Lennartz et al., 2015; Zhu et al., 2019; Sekiya et al., 2020; Wang et al., 2021; Grythe et al., 2014). (Line 101-104)

Thanks for the useful reference information. We described our calculations of halogen emissions in section 2.2 of the manuscript.

**13. Line 135-136: please show the original and scaled halocarbon emissions. Please note that although this is a wildly use approach (i.e., scale to chlorophyll-a), there is no robust relationship between many VSLS and chlorophyll-a (Carpenter et al., 2009; Chance et al., 2014; Liu et al., 2013)**

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**Response:**

The original halocarbon emissions are based on that of Ordóñez et al. (2012). Please see table R1 for the scale factors.

**Table R1(S2).** Global annual fluxes of very short-lived halocarbons reported in previous studies and scale factors of halocarbon emissions used in this study.

Species	Annual flux (Gg/yr)			Scale factor	
	Ordóñez et al. (2012)	WMO low	WMO high	low	high
CHBr <sub>3</sub>	533	126	865	0.24	1.62
CH <sub>2</sub> Br <sub>2</sub>	67.3	62	109	0.92	1.62
CH <sub>3</sub> I	303	176	615	0.58	2.03
CH <sub>2</sub> BrCl	10.0	6.48	9.72	0.65	1
CHBr <sub>2</sub> Cl	19.7	19.6	56.1	1	2.85
CHBrCl <sub>2</sub>	22.6	16.4	22.6	0.73	1
CH <sub>2</sub> ICl	234	--	--	0.58	2.03
CH <sub>2</sub> I <sub>2</sub>	87.3	--	--	0.58	2.03
CH <sub>2</sub> I <sub>2</sub>	116	--	--	0.58	2.03

We agree that the estimation of VSLS emission is very rough.

**14. Line 139: the iodide-driven ozone deposition is coupled with the reactive iodine emission in several recent studies (Karagodin-Doyennel et al., 2021; Pound et al., 2020).**

**Response:**

We thank the reviewer for the references. We are aware of such kind of “couple”, which may be called apparent couple where the two processes are related only through O<sub>3</sub> concentration.

By “couple” we mean the actual couple of the two processes through the aqueous reactions in the sea surface. It is the aqueous reactions that consume O<sub>3</sub> and produce inorganic iodine at the same time. This approach is conducted to develop the parameterization of I<sub>2</sub>/HOI emission by Carpenter et al. (2013) (see their Table

S1).

To avoid confusion, we delete “but current CTMs do not couple these two processes” in the revised manuscript (Line 187-188).

**15. Line 142: Sherwen et al., (2019) showed that the McDonald et al. iodide parameterization underestimates the surface seawater iodide by roughly a factor of 2 on the global scale. Chance et al. is improved but shows wider variability compared to observations.**

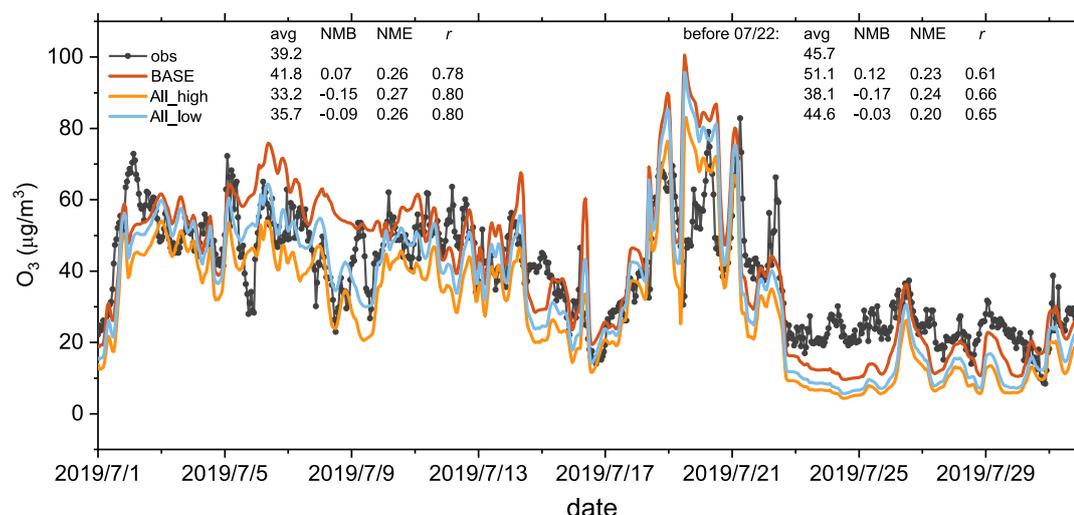
**Response:**

Thanks for the comment. Since the reported iodide values by Sherwen et al., (2019) lie between those calculated values according to parameterization of McDonald et al. (2014) and Chance et al. (2014), we chose the latter two to conduct sensitivity simulations.

**16. Line 150-: The amount of ozone measurements used to demonstrate the performance of this model (Figure S1) is remarkable. But this is less relevant for this study since the majority of the stations are located inland and hence are probably not heavily impacted by the marine halogens. What is directly relevant for this study is, the modeled ozone levels in those sensitivity studies, especially in the All\_High case, and how would these compare to the coastal ozone measurements when the air masses are primarily originated from the ocean.**

**Response:**

Thank you very much for your great comment. We realize that the modeled ozone level is important and add further discussion about it. Please see the response to major comment #2 above. Besides, we add a comparison of simulated and observed O<sub>3</sub> in an island in the Philippine Sea. Please see Fig. S1b in the revised manuscript (Fig. R2 below).



**Fig. R2 (Fig. S1b).** Simulated and measured O<sub>3</sub> concentration at Yonaguni station

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which is a coastal station located in an island of Philippine Sea. The variation of O<sub>3</sub> in July 2019 here is reasonably captured by all the three simulations. Adding the halogen emissions (especially with low emission rates) can noticeably lower the bias for the high ozone concentration and improve the correlation between observation and simulations (i.e., days before July 22).

**17. Line 158: Almost all...? Also, what is considered as benchmark here?**

**Response:**

The benchmark is recommended by Emery et al. (2017). The normalized mean bias in the YRD region exceeds the benchmark value. We rephrase the sentence as [except NMB in the YRD, all these values meet the benchmarks \(Emery et al., 2017\)](#). (Line 214)

**18. Table 3: Note that the daytime average IO reported in Großmann et al. does not exceed 1.5 ppt in the Northwest Pacific (10-40N), although the measurement uncertainty is close to ~1 ppt. Koenig et al., (2020) and Karagodin-Doyennel et al., (2021) also reports IO vertical profiles in the western Pacific in the upper troposphere/lower stratosphere. What does the modeled IO in the upper troposphere look like over the Western Pacific? Could also list a few modeling studies for surface IO (the authors listed a few values from GEOS-Chem for BrO, so might as well). Also please mark on Figure 1 the approximate locations of the studies listed in Table 3 for evaluation.**

**Response:**

Thank you for your valuable comment. We correct the cited values using daily average in Fig. 7 of Großmann et al. (2013). We also add a reference to a previous model study in the Asia-Pacific region (Huang et al. 2020) for modeled IO, but we do not find global model studies that discuss seasonal variation of IO concentration. The study of Huang et al. (2020) indicates a seasonal variation of surface IO in the Western Pacific and in July IO reaches maximum. Besides, we also add some discussion about the difference between PBL and surface XO. Generally, IO in surface layer is larger than PBL average. Therefore, slightly larger modelled IO values than those reported by Großmann et al. (2013) is reasonable (Jul>Oct, surface>PBL). Because we only output surface layer results in All\_low case due to the storage limitation, we cannot update Table 3 by replacing surface IO with PBL IO, and only add discussions in the context. The revised context is as follows:

[In a cruise in October from Japan to Australia, Großmann et al. \(2013\) measured IO, showing that the daytime average of IO concentration ranges from ~0.5 to ~1.5 pptv, with a typical daytime value ~1 pptv. Previous model results showed that surface IO in the Western Pacific has a significant seasonal variation, peaks in summer \(Huang et al. 2020\) and the difference between July and October is about 0.2–0.4 pptv according to their Figs. 3m,p. Therefore, it is expected that our](#)

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simulation values will be slightly larger than the values reported by Großmann et al. (2013). Moreover, since modelled IO also decreases with height in the lower troposphere (see Fig. 2 of Huang et al. (2020)), the surface IO is also expected to be slightly larger than the boundary-layer average of IO. ... (Line 235-241)

For boundary-layer average, the values for IO are lower than surface values by ~0.08 pptv for grid average and by ~0.4 pptv for grid maximum in the Philippine Sea in All\_high case (Fig. 1d) (due to the storage limitation, we did not output upper-layer results in All\_low case). Different from IO, BrO does not decrease with height in the lower ~500m in the study of Huang et al. (2020), and our simulations also show that boundary-layer average of BrO is slightly larger than surface values by ~0.05 pptv (Fig. 1b). (Line 258-262)

For IO in the upper troposphere, because we only output results in the lowest 22 layers, about 3500 m, we cannot discuss modelled values in the UTLS in our manuscript.

**18. Figure 1: Are those in the surface air or averaged in the marine boundary layer? Please clarify. Also the IO color scale used in Figure 1(b) and (d) are inappropriate since very large areas are saturated at 2 ppt already.**

**Response:**

They are in the surface air.

We extend the color scales in those figures.

**19. Lines 197-198: What is this “middle area of the ocean”?**

**Response:**

Modified to “most areas”.

**20. Line 236, 240: photolysis of O<sub>3</sub>: note that the photolysis of O<sub>3</sub> is not really producing OH directly, it is the produced O<sup>1</sup>D reaction with water vapor that generates OH. Please clarify how this P\_OH\_O1D term is calculated.**

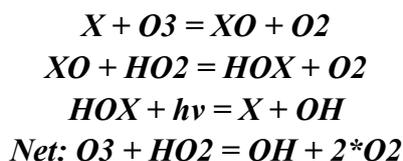
**Response:**

Thanks. “photolysis of O<sub>3</sub>” is short for the OH production originated from O<sub>3</sub> photolysis since in the model only O<sub>3</sub> photolysis can produce O<sup>1</sup>D. We explicate “photolysis of O<sub>3</sub> (through the reaction O<sup>1</sup>D+H<sub>2</sub>O, which will not always be explicitly stated in the following)” in the revised manuscript (Line 314-315) to avoid misunderstanding.

**20. Line 252: “Since HOX is a primary source of OH...” I do not think HOX should**

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*be considered as a primary source of OH. Essentially what it does is converting HO2 to OH:*



**Response:**

Thanks for the comment, and we delete “primary”.

For further discussion, our results indeed indicate that HOX is mainly not a primary source of OH. However, since HOI can be directly emitted, it could be a primary source. Actually, some authors have implied that it is the direct emission of HOI, rather than the cycling of HOI, that is responsible for the increasing of OH induced by iodine (Stone et al. 2018). Nevertheless, it is mainly not the case.

*21. Lines 259-261: I do not understand what the authors mean by “delta\_P\_OH\_HO2 was generally ignored in previous CTM studies”. This term denotes the OH production from HO2 + NO/O3/..., which are some of the most essential reactions in the atmosphere. I doubt these are actually ignored in any major modern CTMs. Please list the models that actually ignores these extremely important reactions. And again, not all box models are observationally constrained.*

**Response:**

We are sorry for the confusion. We do not mean that these reactions are ignored, but that they are ignored in explaining the results. We have deleted this sentence.

*22. Line 265-: this paragraph attempts to explain the striking spatial variability shown in Figure 2 but it does not really deliver a clear answer. Figure 3, as currently shown, does not help with this purpose at all: the sum of panel (a), (e), and (f), should yield panel (g). But the color scales of Panel (f) is poorly chosen (mostly saturated at  $\sim 1e+6 \text{ cm}^{-3} \text{ s}^{-1}$ ), which, I think, is key to explain the spatial discrepancy shown in Panel (g). I would expect that the largely positive delta\_P\_OH\_HOX term is partially compensated in Bohai Sea and the Sea of Japan but completely overturned in the Yellow Sea and East China Sea, by the sum of delta\_P\_OH\_O1D and delta\_O\_OH\_HO2. In light of this, I would suggest the authors tweak the color scales in Panels (a), (e), and mostly importantly (f). Could remove Panels (b), (c), (d), and (h) and describe in the text that these pathways are virtually neglectable.*

**Response:**

Thanks for the suggestion. We extend the colorbars in the figures and remove (b), (c) and (d) in Fig. 3.

The different signs in different areas in Fig. 3(g) is caused by the competition of (a)+(e) and (f) *from definition* if we ignore the other pathways because the results of IRR are additive. They do not clearly answer the question why the spatial

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pattern of (g) is like that, but they provide information that the pathways themselves have monotonic effects. Based on this, we further explore the effect of different halogen species and finally focus on iodine chemistry which have very similar  $\Delta P_{OH\_O1D}$ ,  $\Delta P_{OH\_HO2}$  and  $\Delta P_{OH\_HOX}$  with All\_high.

**22. Line 285 & Line 307: It remains unclear in the current version of the manuscript that how debromination from sea salt is implemented in this model, which, is the dominant reactive bromine source in the troposphere (Wang et al., 2021; Zhu et al., 2019). Please compare the sea salt debromination rates derived from this work to the literature values.**

**Response:**

The debromination from SSA in CMAQ5.3 are implemented as follows (Sarwar et al. 2019):



The reaction constant for these heterogeneous reactions is of the form  $k = \left(\frac{d}{2D} + \frac{4}{c\gamma}\right)^{-1} A$ , where d represents the effective diameter, D represents the diffusivity (of the gases) in air, c is the mean molecular velocity, A is the aerosol surface area concentration, and  $\gamma$  is the reactive uptake coefficient.  $\gamma$  of HOBr, INO<sub>3</sub>, INO<sub>2</sub>, and HOI are 0.1, 0.01, 0.2, and 0.01, respectively, but the yield of gaseous Br species is not 1 because these gases do not only react with Br<sup>-</sup>. Consequently, the “effective”  $\gamma$  for Br<sup>-</sup> are 0.02, 0.005, 0.01, and 0.005 (i.e., 20%, 50%, 50%, and 50%, the remaining reacts with Cl<sup>-</sup>, see Table S3 in Sarwar et al. (2019)).

For the last three uptake coefficients, they are the same as those in Wang et al. (2021a). But the “effective”  $\gamma$  for Br<sup>-</sup> are smaller in Wang et al. (2021a) because only 15% of INO<sub>3</sub>, INO<sub>2</sub>, and HOI react with Br<sup>-</sup> and the other 85% react with Cl<sup>-</sup> (see R10–12 in Wang et al. (2021a)). Therefore, the debromination rate through RS1–RS4 should be higher. However, since “[m]ost of the SSA debromination in the model is from Reaction (R1)” (Zhu et al. 2019) (R1 is RS1 here), the most important parameter is  $\gamma$  of HOBr.

In our model, the uptake of HOBr is simply treated like INO<sub>3</sub>, INO<sub>2</sub>, and HOI. However, in the studies of Zhu et al. (2019) and Wang et al. (2021a), more complicated treatment of the uptake of HOBr is implemented. First, HOBr can react with dissolved SO<sub>2</sub> in addition to Cl<sup>-</sup> and Br<sup>-</sup>. Second,  $\gamma$  of HOBr is a function of ion concentrations and pH, instead of a constant. Third, much more HOBr reacts with Br than Cl (9:1 when Br/Cl > 5 × 10<sup>-4</sup> which is the case in our simulations in

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the whole domain, instead of 2:8).

It is not clear what values of  $\gamma$  of HOBr are as a function of ion concentrations and pH. Previous GEOS-Chem studies used constant  $\gamma$ , but both 0.1 and 0.2 were used (Fernandez et al. 2014; Ordóñez et al. 2012; Parrella et al. 2012). Our model follows that of Fernandez et al. (2014), taking  $\gamma=0.1$ . Updating  $\gamma$  as a function of ion concentrations, Schmidt et al. (2016) showed larger  $\text{Br}_y$  source from debromination than that of Parrella et al. (2012) ( $1620 > 1420 \text{ GgBr/yr}$ ). Then, we may infer that the variable  $\gamma$  has a larger annual average than the constant 0.2 in Parrella et al. (2012). The resulting higher BrO leads to the exclusion of debromination of SSA in some GEOS-Chem studies (e.g., Sherwen et al. 2016b; Stone et al. 2018), which in turn results in the inclusion of the reaction  $\text{SO}_2+\text{HOBr}$  that is intended to consume HOBr (compete with  $\text{HOBr}+\text{Br}^-$ ). The net result of these two opposite updates (increase HOBr uptake but decrease  $\text{Br}_2$  release) of GEOS-Chem model is unclear, and we simply assume it is null (i.e., the increase and decrease cancel out each other in terms of Br activation). Then in previous GEOS-Chem studies  $\gamma$  of HOBr for  $\text{Br}^-$  and  $\text{Cl}^-$  is usually 0.2 as in Parrella et al. (2012). From this consideration, the model in our study probably underestimates debromination rate by 50%. Furthermore, the yield of  $\text{BR}_2$  is significantly underestimated compared to those studies, resulting a further underestimation of debromination rate.

However, the exclusion of debromination of SSA in several previous GEOS-Chem studies (Schmidt et al. 2016; Sherwen et al. 2016b; Stone et al. 2018) but without decreasing BrO burden (Zhu et al. 2019) indicates that there are more complicated interactions between different reactive bromine species ( $\text{Br}_y$ ). Since Br chemistry influences OH mainly through consuming  $\text{O}_3$  (Stone et al. 2018) which will produce BrO (and BrO is mainly produced from  $\text{Br}+\text{O}_3$ ), constraining modelled BrO is enough for our purpose in this study. Since there are very few measurements in the Western Pacific, the constrain in our study is inadequate. But more measurements are needed for further improvement of modelling.

Because the story of the development of debromination from SSA in previous GEOS-Chem study is very complicated, we only briefly mention it in our revised manuscript:

Recent model GEOS-Chem studies improved the uptake of HOBr substantially, but the two major revisions have opposite effects on BrO: increasing HOBr uptake by using more sophisticated parameterizations (Schmidt et al. 2016) and decreasing  $\text{Br}_2$  yield by adding competition reactions of HOBr with S(IV) (Chen et al. 2017; Wang et al. 2021b; Zhu et al. 2019). The uptake of HOBr in our study is simply parameterized with a constant reactive uptake coefficient 0.1 (Sarwar et al. 2019), which may result in a lower debromination rate. However, since Br chemistry influences OH mainly through the consumption of  $\text{O}_3$  (Stone et al. 2018), the constraining on modelled BrO is sufficient for our purpose. as shown in 3.1, modelled BrO is comparable to previous studies (Zhu et al. 2019), indicating the

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update of HOBr chemistry may not be critical to our results, but more measurements of BrO with seasonality information are needed for further evaluation of the impacts of Br chemistry. (Line 598-609)

**23. Line 287: ... the impact of inorganic iodine is stronger/larger/more pronounced than...**

**Response:**

Revised as suggested.

**24. Line 314-: Sure Cl itself is a strong oxidant but why would Cl oxidation affect OH radical production? Is it thru RO2  $\rightarrow$  HO2  $\rightarrow$  OH channel? Please clarify.**

**Response:**

Yes, it is. We discuss this in [line 433-435](#) when illustrating the effect of SSA Cl chemistry in the revised MS.

**25. Line 395: the point of having debromination is not to solve “excessive BrO”. Debromination is, however, the largest net source of reactive bromine in the global troposphere (Wang et al., 2021; Zhu et al., 2019). Please compare the sea salt debromination rate derived from this work to the literature values.**

**Response:**

We agree that debromination is the largest net source of reactive bromine in the global troposphere and we did not mean that debromination is to solve “excessive BrO”. Instead, the excluding of debromination in many previous studies is used to solve the “excessive BrO” (Schmidt et al. 2016; Sherwen et al. 2016b). Recent studies solve the problem by introducing heterogeneous reactions of HOBr+S(IV) and therefore recover debromination. Our mechanism does not contain the heterogeneous reactions of HOBr+S(IV). If they are included, BrO concentration would be substantially decreased (BrO burden decreases by more than 50% in the study of Chen et al. (2017)) (Chen et al. 2017; Wang et al. 2019; Zhu et al. 2019).

Detailed comparison of the sea salt debromination rate in this work and that in the literature have been clarified in the response to comment #22 above.

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## Reviewer #2:

### Major:

*1. The authors present a study of the effects of halogen chemistry on the concentrations and production rates of OH radicals in the East Asia region in July 2019 using the CMAQ model with WRF meteorology. The methodology applied is appropriate to the study, and the results will be of interest to the atmospheric science community.*

*The emission schemes and chemical mechanisms for halogens (Cl, Br, and I) employed in the model are generally well described, and there is some comparison of model results with observations of halogen species where these are available. However, the manuscript would benefit from some additional discussion of the uncertainties in the mechanisms with a view to highlighting which processes in the model should be targeted for improvements that will reduce model uncertainty.*

### Response:

Thanks for the suggestion. We extend the discussion in section 3.5 Limitations to include some discussion about mechanism-improving direction. Please see the full discussion in the revised section 3.5. The following gives a simpler description:

For Cl chemistry, the most important mechanism that is not well known is the activation of particulate Cl. The oxidation of VOCs by Cl atom is also of significant interest, especially for SOA formation.

For Br chemistry, the debromination of SSA underwent significant revision in recent years and current mechanism may well represent the real atmospheric process. However, the excluding of SSA debromination through HOBr+Br<sup>-</sup> reaction in several previous GEOS-Chem studies (Schmidt et al. 2016; Sherwen et al. 2016; Stone et al. 2018) but without decreasing BrO burden (Zhu et al. 2019) indicates that there are more complicated interactions between different reactive bromine species (Br<sub>y</sub>).

For iodine chemistry, recent measurements indicate that the uptake of HOI is much more rapid than previously known (Tham et al. 2021). More modeling tests are needed to explore the implication of this faster uptake of HOI.

*2. Similarly, how do uncertainties in measurements (or in the availability of measurements) impact tests of model performance and the model results? Are there key species or locations which should be targeted for future observations that would help to validate models?*

### Response:

Since the influence of halogens on OH usually relate to XO, it is critical to validate

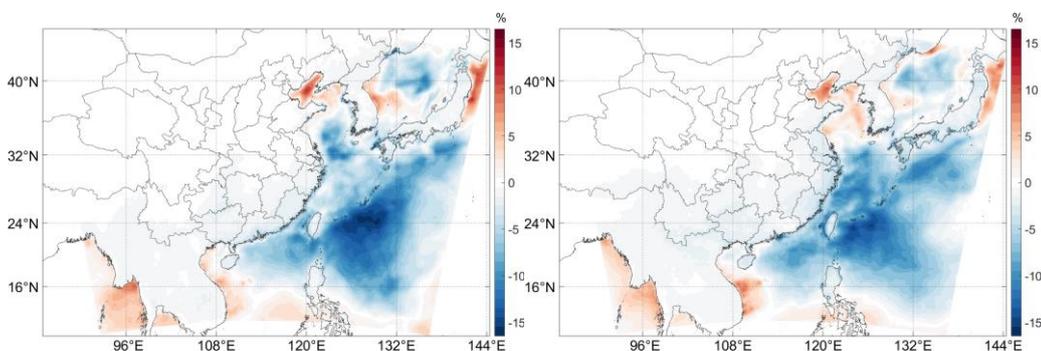
the modelled XO. However, current observations of XO (and other reactive inorganic halogen species) are very sparse, more observations especially over the ocean are needed. In particular, the seasonality of XO is urgently needed because both BrO and IO have large seasonal variation. For IO, since we modelled very high concentration in the coastal waters but without observations to constrain the modeling, more observations in coastal waters are needed.

Please see more details in section 3.1 and 3.5.

**3. Can the authors comment on any expected seasonal effects? How representative are the conditions in July 2019 of other summer months and of other years?**

**Response:**

August 2019 has almost identical monthly averaged distributions of halogen-induced  $\Delta P_{OH}$  and  $\Delta OH$  as that of July. Therefore, it is expected that different months in summer are similar.



**Fig. R1.** Relative change of  $P_{OH}$  in July (left) and August (right), 2019.

For other years, we argue as follows: the patterns are mainly controlled by SSA and H2/HOI, whose emissions are controlled by wind speed only (SSA) or wind speed, O<sub>3</sub> concentration and SST (H2/HOI). We believe that monthly averaged WS and SST in 2019 should be representative for other years because they are only controlled by low-frequency variations of the climate system. But for O<sub>3</sub> concentration, the dramatic decrease of anthropogenic emissions of its precursors could influence the representative. However, since this study is a mechanism study, and the role is detailed discussed in the revised manuscript, the change of O<sub>3</sub> concentration due to emission reduction could be inferred.

**3. Are there any impacts of halogens on OH loss processes as well as processes involved in the production of OH.**

**Response:**

Yes, there is. The exclusive loss pathway of OH is reactions with VOCs. Since Cl atom can react with some VOCs at similar or even faster rate than OH+VOCs, Cl atom can influence the OH loss. But the impact is very small due to the low concentration of Cl atoms.

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**4. Is it possible to comment on the wider significance of the results? What do the results imply about our understanding of methane lifetimes for example?**

**Response:**

Thanks for your great comment. It is indeed of great interest on how the halogen chemistry influence CH<sub>4</sub> lifetime, which has been discussed by several previous studies by global models. Briefly, since OH is generally decreased by halogens at the global scale, the CH<sub>4</sub> lifetime is generally increased by halogen chemistry. (see e.g. Stone et al. 2018, Wang et al. 2021). However, in a regional model it is difficult to discuss lifetime of CH<sub>4</sub>, which is treated as a long-lived species and its concentration is constant in CMAQ.

But, some discussion is possible for short-lived species as they have significant spatial variation and the focused domain may be an important source of the species. We refer the reviewer to Wang et al. (2021) for more information of this kind. We add some new runs to discuss the interactions of some anthropogenic pollutants with halogens in the revised MS (Line 514-558).

**Specific comments:**

**1. Line 33: HO<sub>2</sub> should not really be considered as a source of OH owing to its production via OH reactions.**

**Response:**

We agree this statement in the sense that HO<sub>2</sub> is not a primary source of OH. We revise our manuscript as follows:

When there is abundant NO, as typically in the polluted continental atmosphere, peroxy radicals (RO<sub>2</sub>, and HO<sub>2</sub>) will be formed by the oxidation of hydrocarbons by OH, and will form OH again in the reaction with NO. This HO<sub>x</sub> (=OH+HO<sub>2</sub>) cycling maintains a high OH concentration that cannot be achieved by primary sources alone. (Line 48-51)

**2. Line 37: Define NO<sub>x</sub> and the concentration range used to define the low NO<sub>x</sub> regime. Note that the studies mentioned in which modelled OH concentrations are underestimated typically have both low NO<sub>x</sub> and high biogenic VOCs. It's not clear that these studies are relevant to marine regions.**

**Response:**

We agree that those studies are probably not relevant to marine regions and we revise our manuscript:

Due to the complexity of the HO<sub>x</sub> chemistry, the sources and sinks of OH are not fully understood. For example, recent studies showed that when NO<sub>x</sub> concentration is very low there may be missing sources of OH. (Fittschen et al. 2019; Fuchs et al. 2013; Hofzumahaus et al. 2009; Lelieveld et al. 2008; Lu et al.

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2019; Rohrer et al. 2014; Stone et al. 2012; Tan et al. 2019; Whalley et al. 2021). Besides, HO<sub>x</sub> chemistry can interact with other oxidizers in the atmosphere in specific circumstances. (Line 51-59)

**3. Lines 56-69: The chemistry HO<sub>2</sub> + XO and HO<sub>2</sub> + NO was included in previous studies and the impacts were thus considered as part of the overall effects.**

**Response:**

Sorry for the misleading. We agree that the reactions are included in previous studies and the overall effect there reflected the influence of these reactions. Our point is that only specific pathways have been considered in the interpretation of the model results, but some pathways are not considered.

**4. Line 100: Is a 10 day period appropriate to spin-up any long-lived species in the model?**

**Response:**

Spin-up in regional models is for I.C and B.C. which is provided by global models. Besides, an extended simulation to August does not invoke any significant change of the results, we can say that for our purpose, 10-day spin-up is adequate.

**5. Line 113: It would be preferable to reference a peer-reviewed result rather than a figure in a preprint version.**

**Response:**

Thanks. Revised as suggested.

**6. Lines 237, 252, 265: Although HO<sub>x</sub> photolysis is potentially a primary source of OH, it may also be considered a secondary source if significant HO<sub>x</sub> is produced via HO<sub>2</sub> + X since HO<sub>2</sub> is primarily produced via OH chemistry. It would be helpful if the authors could comment on the relative importance of chemical production of HO<sub>x</sub> and direct emission of HO<sub>x</sub>. What fraction of OH is produced via photolysis of HO<sub>x</sub>?**

**Response:**

Thanks for your valuable comment. The majority of HO<sub>1</sub> is actually secondary, see Fig. S7. Therefore, we delete “primary” in lines 237 and 252.

**7. Line 242: Please clarify the meaning of FORM + O. Is there any impact of halogen chemistry on formaldehyde?**

**Response:**

Cl will react with formaldehyde, and the production of formaldehyde will be influenced.

We grouped the other sources than the three main sources (P<sub>OH\_O1D</sub>, P<sub>OH\_HO2</sub>, P<sub>OH\_HOX</sub>) as P<sub>OH\_other</sub> and since it is very small, we do not discuss them in the

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revised manuscript.

**8. Line 259: Changes in OH and HO2 have been considered as part of the net result in previous CTM studies, it isn't really correct to say that these changes were ignored.**

Thank you for your comment. We delete the sentence.

**9. Line 260: The box model studies do provide accurate model results, but they are typically directed at different processes and different timescales. It is not really correct to say that a model is not accurate.**

**Response:**

Thank you. We agree. We delete the sentence.

**10. Line 368: Are the changes to the photolysis of HOX and HO2 + Y linked via HO2 + X?**

**Response:**

Yes, they are. They compete with each other for HO<sub>2</sub>. Also, Y (NO and O<sub>3</sub>) can indirectly link these two because the product of HOX photolysis, X, will consume O<sub>3</sub> and have complicated influence on NO<sub>x</sub>. We add the reactions in the revised MS as bellow ([Line 364-367, 371-372](#)).



**11. Line 302 onwards: Please show the charges on ionic species.**

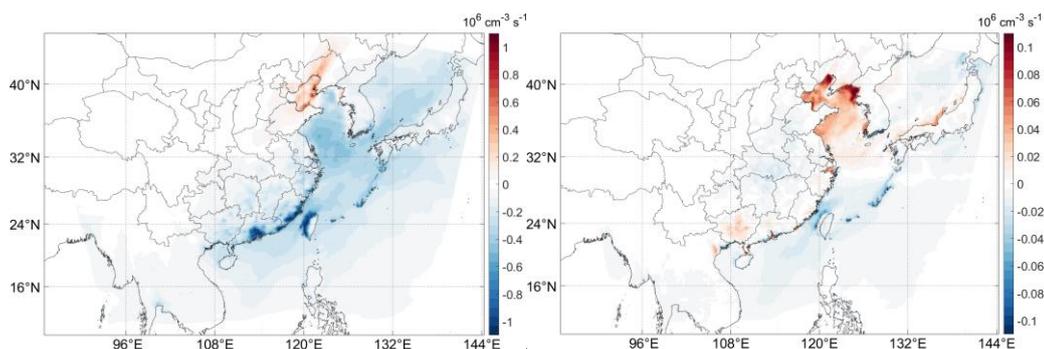
**Response:**

Revised as suggested.

**12. Line 411: Is it possible to perform any sensitivity analysis to HO2 uptake?**

**Response:**

Yes. We conduct sensitivity simulations to evaluate the impact of HO<sub>2</sub> uptake under the influence of marine halogen chemistry. Surprisingly, the uptake of HO<sub>2</sub> does not significantly change the impact of SSA emission on the OH production as shown in Fig. R3 that with or without HO<sub>2</sub> uptake have very small difference in the SSA-induced ΔP<sub>OH</sub>. Therefore, we delete relevant discussion in section 3.5.



**Fig. R3.** Change of  $P_{OH}$  caused by SSA emission with  $HO_2$  uptake (left, see also Fig. 4a for that without  $HO_2$  uptake in the main text) and with minus without  $HO_2$  uptake (right). Note the different scales.

*There are also a number of language improvements that should be corrected. Some of these are listed below:*

*Title: This would read better as ‘on OH radicals’ or ‘on the OH radical’.*

*Line 9: ‘Hydroxyl (OH) radical... OH’ to ‘hydroxyl (OH) radicals... The OH’.*

*Line 11: ‘OH level’ to ‘OH levels’.*

*Line 16: ‘response of OH’ to ‘response of the OH’.*

*Line 23: ‘while increase’ to ‘while increasing’.*

*Line 25: ‘the southern’ to ‘southern’.*

*Line 26: ‘the coastal’ to ‘coastal’.*

*Line 31: ‘Hydroxyl’ to ‘The hydroxyl’.*

*Line 32: Define VOCs, ‘produce’ to ‘producing’.*

*Line 34: ‘O1D’ to ‘O(1D)’, ‘At urban’ to ‘In urban’.*

*Line 44: ‘impact’ to ‘impacts’, ‘The marine-emitted halogen’ to ‘Marine-emitted halogens’.*

*Line 50: ‘long-term’ to ‘long-lived’.*

*Line 53: Define HOx.*

*Line 54: ‘CTMs studies’ to ‘CTM studies’.*

*Line 81: It would help to define CMAQ and WRF in full.*

*Line 89: ‘mechanisms’ to ‘mechanism’.*

*Line 90: ‘Rosenbrock’ to ‘The Rosenbrock’.*

*Line 105: ‘inline’ to ‘online’?*

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*Line 134: 'global annual' to 'by global annual'.*

*Line 161: 'though' to 'although', 'in-situ' to 'in situ', 'area is' to 'area are'.*

*Line 164: 'BrO and IO very' to 'BrO and IO are very'.*

*Line 165: 'IO concentration' to 'the IO concentration'.*

*Line 166: 'Western Pacific' to 'the Western Pacific'.*

*Line 171: 'largest' to 'the largest', 'while smallest' to 'and the smallest'.*

*Line 184: 'average' to 'the average'.*

*Line 189: 'related to O3' to 'related to the O3'.*

*Lines 203, 204, & 207: 'slight' to 'a slight'.*

*Line 205: 'decrease' to 'a decrease'.*

*Line 206: 'increase' to 'an increase'.*

*Line 208: 'while increase' to 'while increasing'.*

*Line 225: 'literature' to 'the literature'.*

*Line 235: 'CB6' to 'the CB6'.*

*Line 236: 'source' to 'sources'.*

*Line 251: 'whole' to 'the whole'.*

*Line 252: 'daytime' to 'the daytime'.*

*Line 311: 'daytime maximum' to 'the daytime maximum'.*

**Response:**

Thanks a lot. Revised as suggested.

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**Reviewer #3:**

## **Major**

*1. This manuscript analyzes regional model simulation results regarding the impact of tropospheric halogen chemistry (Cl, Br, and I) on the production rates and concentrations of OH over East Asia and Western Pacific during summer. Three major pathways, i.e., O<sub>3</sub> photolysis rate, HOX photolysis, and HO<sub>2</sub>+Y were identified and the changes were quantified per emission types (SSA, inorganic iodine, and halocarbons) and their associated processes (chemistry, radiation, and deposition). Although not proposing new processes, the authors describe the overall impact in an integrated manner and then their attribution to individual processes. The Western Pacific low-latitude region is with fairly high sea surface temperature during summer and thus potentially high impact of iodine chemistry (due to high [I<sup>-</sup>] in the surface seawater) is expected. The findings are mostly reasonable and the logical flow of the manuscript appears sound.*

*Nonetheless, there are several points needing clarification. First, additional fundamental information of this study is required for justification. For example, a table of chemical reactions relevant to tropospheric halogen chemistry taken into account in the simulations is needed at least in the supplement. Maps of the assumed SSA, HOI and halocarbon fluxes will also help understanding. Typical air transport patterns during July 2019 should be described.*

## **Response:**

Thank you very much for your suggestions. Tables of full halogen chemical reactions have been provided by Sarwar et al. (2012) (for Cl chemistry) and Sarwar et al. (2019) (for Br and I chemistry) in previous studies. we add more description about the chemical mechanism in our revised manuscript as follows:

The chemical mechanism adopted here is CB6r3m released in CMAQv5.3, which is updated by adding halogen chemistry to CB6r3 mechanism based on the work of Sarwar and co-workers (Sarwar et al. 2012; Sarwar et al. 2014; Sarwar et al. 2015; Sarwar et al. 2019). Details of the gaseous reactions and heterogeneous reactions can be found in the recent work of Sarwar et al. (2019) (see also Table S1). (Line 131-135)

HOI and I<sub>2</sub> emission rates are added in Fig. 8 in the revised manuscript. SSA emission rates are added in Fig. S6. Halocarbon emissions are concentrated in the coastal waters, and since we did not discuss them much, we do not add the emission map in our revised manuscript.

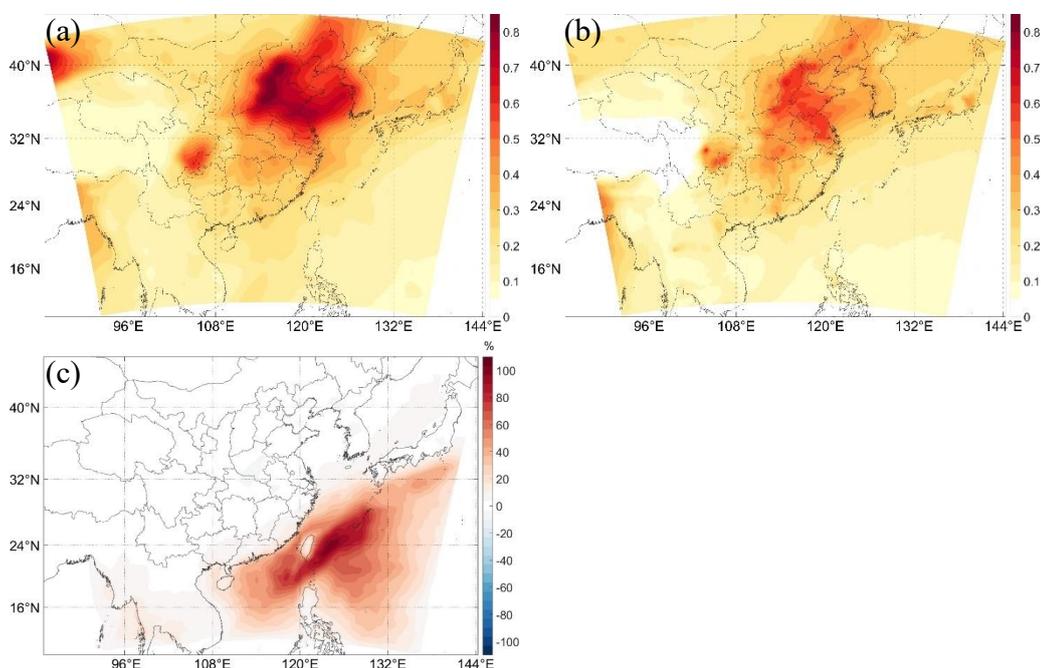
For the typical air transport patterns, since the domain is under the impact of East Asia summer monsoon, the general wind field over the ocean is northward. We add the average wind field in Fig. S1.

2. clarification is necessary for some processes. For example, I am afraid that the impact of sea spray aerosols on  $J(O^1D)$  (Fig. S5, Fig. 6a) is a bit too large. The aerosol optical depth and assumed single scattering albedo in the model need evaluation. Also I do not understand why the  $InorgI_{chem}$  can result in "negative" values over the Philippine Sea, although some explanation is given in lines 379-382.

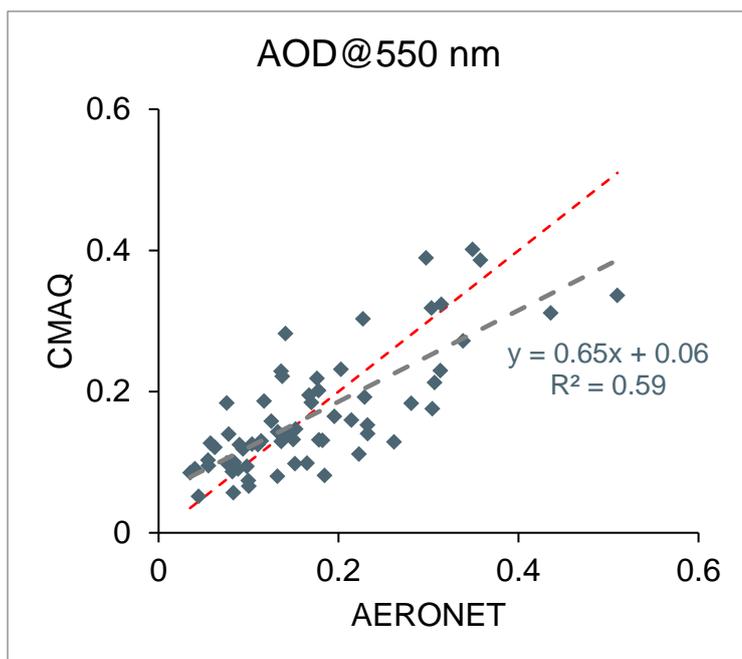
**Response:**

Thank you for your comment. The model simulated light extinction by aerosol types. We conduct a validation for the aerosol optical depth (AOD). Comparison of daily modeled AOD@550nm in All\_high case and AERONET AOD (550nm calculated from 500nm using Angstrom exponent) at four available island stations (north to south: Fukue, Okinawa\_Hedo, Dongsha, and Manila is presented in Fig. R2. The spatial distribution of AOD in average is also presented in Figs. R1,2. The spatial and temporal comparison show a pretty good performance of the AOD stimulation.

The SSA-induced increase of AOD (Fig. R1c) over the ocean is very large probably due to the low background AOD. The impact of SSA on  $J(O^1D)$  is generally less than 4% (Fig. S5a). Fig. 6a contains the impact of  $O_3$  decrease induced by the decrease of  $J(NO_2)$ , not just the impact of  $J(O^1D)$  decrease. The large decrease of daytime  $P_{OH}$  (see specific question 16) is in the early morning and late afternoon,



**Fig. R1.** Spatial distribution of (a) MERRA-2 (downloaded from [https://disc.gsfc.nasa.gov/datasets/M2TMNXAER\\_5.12.4/summary?keywords=MERRA-2%20AOD](https://disc.gsfc.nasa.gov/datasets/M2TMNXAER_5.12.4/summary?keywords=MERRA-2%20AOD)) and (b) modelled monthly average of AOD, and (c) relative change of AOD due to the emission of SSA ((All\_high-BASE)/BASE).



**Fig. R2.** Comparison of daily modeled AOD@550nm in All\_high case and AERONET AOD (550nm calculated from 500nm using Angstrom exponent) at four available island stations (north to south: Fukue, Okinawa\_Hedo, Dongsha, and Manila, [https://aeronet.gsfc.nasa.gov/cgi-bin/webtool\\_aod\\_v3?stage=2&region=Asia](https://aeronet.gsfc.nasa.gov/cgi-bin/webtool_aod_v3?stage=2&region=Asia)).

For iodine chemistry and the negative impact in Philippine Sea, we add discussion in [Line 481-558](#):

*3, readability of the manuscript should be improved, as very similar figures (from Figure 2 to 7) appear from one to another. Overall, the manuscript is acceptable after major revisions, responding to the points raised above and to specific comments listed below.*

**Response:**

Thanks for your comment. We add more descriptions in the figure captions. We also add a table for the cross reference of figures and cases in SI:

**Table R1 (S4). Cross reference between cases and figures in this study.**

Figures	Cases
Fig. 1	All_high
Fig. 2	All_high – BASE

	All_low – BASE
Fig. 3	All_high – BASE
Fig. 4	(a)–(d) SSA: SSA – BASE (e)–(h) InorgI: InorgI – BASE (i)–(l) HaloC: HaloC – BASE (m)–(p) interaction: All_high – SSA – InorgI – HaloC + 2BASE
Fig. 5, decomposition of Figs. 4a–d	(a)–(d) SSA_phy: SSA_phy – BASE_phy (e)–(h) SSA_chemCl: (SSA_Cl – BASE) – (SSA_phy – BASE_phy) (i)–(l) SSA_chemBr: SSA – SSA_Cl
Fig. 6	Corresponding values in Figs. 5 and 7, divided by BASE
Fig. 7, decomposition of Figs. 4e–h	(a)–(d) O <sub>3</sub> depo: InorgI – InorgI_chem (e)–(h) InorgI_chem: InorgI – BASE
Fig. 8	All_high
Fig. 9	(a) 1/2 iodine: InorgI_chemIhalf – InorgI_chem (b) 5×O <sub>3</sub> : (InorgI_chemPHIL5 – BASE_PHIL5) – (InorgI_chem – BASE) (c) 5×O <sub>3</sub> : BASE_PHIL5 – BASE

## Specific comments:

1. Line 20. Show what are the "three" major pathways in Abstract.

### **Response:**

Modified as suggested.

2. Line 22. The increased ozone deposition due to enhanced I- ion levels in the surface seawater would be rather "chemical" than physical?

### **Response:**

It is chemical in seawater. Atmospheric chemistry more often treats dry deposition, no matter how it happens, as physical.

3. Line 41. What are the "artificial" and "mechanistic" pathways?

### **Response:**

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What we mean “Artificial” is result-based modification to chemical mechanisms. That is, in order to get such a result, what reactions are needed, or what reaction rate constant need to change. For example, researchers just added RO<sub>2</sub>+RO<sub>2</sub> reactions to get the right (observation-consistent) P<sub>OH</sub>, but do not have sufficient support to consider what RO<sub>2</sub> and how are they involved. In contrast, “mechanistic” pathways need information about what RO<sub>2</sub> and how the reactions happen (chemical kinetics). To avoid confusing, we delete relevant content in the revised manuscript.

**4. Line 50. longer-lived?**

**Response:**

*Revised as suggested.*

**Response:**

Revise as suggested.

**6. Line 52. It is not box models that are to be accused. Maybe "constraining O<sub>3</sub> levels in the model" causes the difficulty that the authors described.**

**Response:**

Thanks for the comment. We modify our manuscript as follows:

In a box model, when the long-lived species such as O<sub>3</sub> are observation-constrained, it cannot reflect the complete influence of halogens, which probably result in the different results between box models and CTMs (Stone et al. 2018). Therefore, special attention needs to be paid when using box models to quantify or explain the complicated impacts of halogen species on the HO<sub>x</sub>-NO<sub>x</sub>-O<sub>3</sub>-VOCs chemistry. (Line 88-91)

**7. Lines 57 and 260. I believe previous CTM studies implicitly take the impact from HO<sub>2</sub> into account, unless they constrain HO<sub>2</sub> levels to observations.**

**Response:**

Thank you for your comment. We delete the sentences.

**8. Line 77. What are "its extreme uncertainties"?**

**Response:**

Revised to “the largest or the smallest emission rates that have been used or reported in previous studies”. (Line 117)

**9. Line 90. List tropospheric halogen chemistry reactions from the CB6r3m mechanism in a supplementary table. Are they identical to those involved in GEOS-**

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*Chem or other recent studies (e.g., Sherwen et al., 2016, Stone et al., 2018, Wang et al., 2021), which are cited in line 202 and compared?*

**Response:**

Thanks. The halogen reactions from the CB6r3m mechanism are listed in the revised SI (Table S1). They are not entirely identical, but contain the similar reactions, especially those considered important as there are many cross references (for example, the SSA debromination reactions except HOBr+Br<sup>-</sup> in the three studies cited and in our study are the same).

**10. Lines 99-100. The typical air mass transportation pattern for this region during July 2019 should be described.**

**Response:**

Thanks. Added as suggested. Please see the detailed in the response to major comment #1.

**11. Line 140. I believe these two processes are coupled in Sekiya et al. (2020).**

**Response:**

We thank the reviewer for the reference. We are aware of such kind of “couple”, which may be called apparent couple where the two processes are related only through O<sub>3</sub> concentration.

By “couple” we mean the couple of the two processes through the aqueous reactions in the sea surface. It is the aqueous reactions that consume O<sub>3</sub> and produce inorganic iodine at the same time. This approach is conducted to develop the parameterization of I<sub>2</sub>/HOI emission by Carpenter et al. (2013) (see their Table S1).

To avoid confusion, we delete “but current CTMs do not couple these two processes” in the revised manuscript (Line 187-188).

**12. Table 1. One idea would be to add one column in the right to indicate in which Figure the results of the cases are studied.**

**Response:**

Thanks for the suggestion. We add a table (Table S4) in the revised manuscript. Please see the major comment #3 above

**13. Line 242. Explain what FORM+O is.**

**Response:**

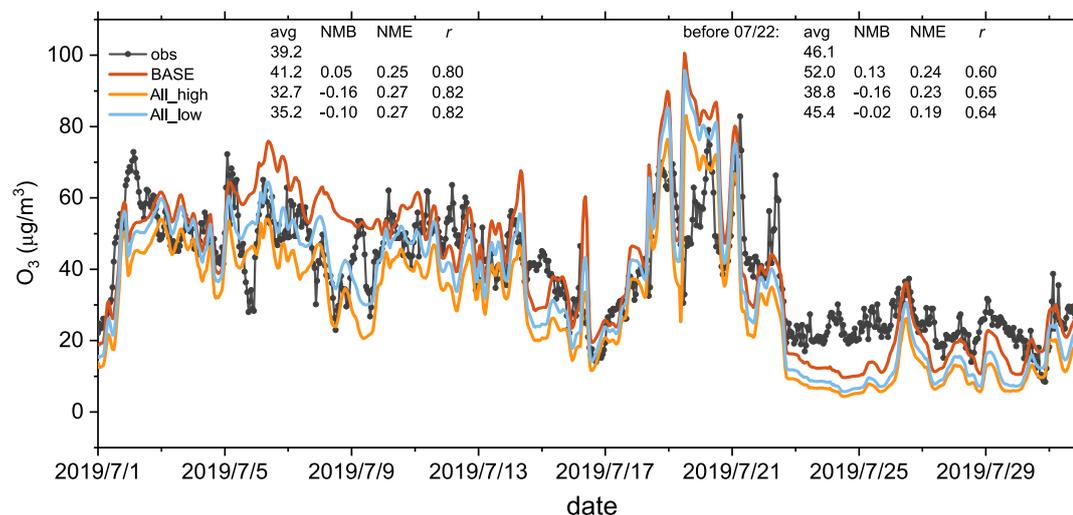
It is the reaction of formaldehyde with oxygen atom. Since all the pathways other than the three main are not important, we delete the details about them.

**14. Section 3.1. The model performance is only checked with O<sub>3</sub> monitoring over the continent. It would be useful to compare the simulation results also with O<sub>3</sub>**

observations at Yonaguni available from <http://ebas.nilu.no>.

**Response:**

Thanks for this very useful information. We add the comparison of simulated and observed O<sub>3</sub> at Yonaguni in the revised manuscript. Please see Fig. S1b in the revised manuscript.



**Fig. R4 (Fig. S1b).** Simulated and measured O<sub>3</sub> concentration at Yonaguni station which is a coastal station located in an island in the Philippine Sea. The variation of O<sub>3</sub> in July 2019 here is reasonably captured by all the three simulations. Adding the halogen emissions (especially with low emission rates) can noticeably lower the bias for the high ozone concentration and improve the correlation between observation and simulations (i.e., days before July 22).

**15. Figures 3-7.** In their figure captions, some more explanation should be included, to clarify cross linkage of the figures. For example, Figure 3 caption could include that they are breakdown of Figure 2a down to processes. Figure 4 would be the breakdown of Figure 3g, a, e, and f. etc.

**Response:**

Thank you very much for your valuable suggestion. We revise the figure captions following the suggestion.

**16. Lines 305 and 312 and Fig. S5.** I am afraid that the impact of sea spray aerosols on  $J(O^1D)$  and then  $P(OH)$  (close to 30% for daytime maximum) is a bit too large. The aerosol optical depth and assumed single scattering albedo in the model need evaluation.

**Response:**

Thanks for pointing out this. The decrease of  $P_{OH}$  is not only caused by the decrease of  $J(O^1D)$ , but also the decrease of O<sub>3</sub> concentration that is probably caused by the decrease of  $J(NO_2)$ , because  $P_{OH\_O1D} \propto J(O^1D) \times O_3$ . Besides, 30%

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is for all the daytime hourly  $\Delta_r P_{OH}$ , which peaks in the late afternoon or early morning when  $P_{OH}$  is low, not for the peak  $P_{OH}$ . We are sorry for the confusion and we modify our expression from “with daytime maximum close to 30%” to “hourly  $\Delta_r P_{OH}$  up to 30% in daytime”. Please see more details about the evaluation of AOD in the major comment #2.

**17. Line 370. What is the process that "iodine" diminishes the photolysis of O3?**

**Response:**

Iodine species simply destruct O3, and photolysis (not photolysis rate constant) of O3 is positively related to O3 concentration.

**18. Lines 379-382. Why can the InorgI\_chem result in "negative" values over the Philippine Sea? I believe that the photolysis of HOI always tend to "increase" OH and thus should have positive values. Coupling with air mass transport may produce this type of feature? Clarification is needed.**

**Response:**

Please see the major comment #2 above.

**19. Line 392. Rely much on the current halogen chemistry**

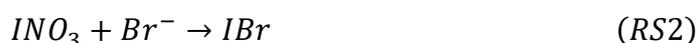
**Response:**

Revised as suggested.

**20. Line 395. The authors should explain how the debromination is included.**

**Response:**

The debromination from SSA in CMAQ5.3 are implemented as follows (Sarwar et al. 2019):



The reaction constant for these heterogeneous reactions is of the form  $k = \left(\frac{d}{2D} + \frac{4}{c\gamma}\right)^{-1} A$ , where d represents the effective diameter, D represents the diffusivity (of the gases) in air, c is the mean molecular velocity, A is the aerosol surface area concentration, and  $\gamma$  is the reactive uptake coefficient.  $\gamma$  of HOBr, INO<sub>3</sub>, INO<sub>2</sub>, and HOI are 0.1, 0.01, 0.2, and 0.01, respectively, but the yield of gaseous Br species is not 1 because these gases do not only react with Br<sup>-</sup>. Consequently, the “effective”  $\gamma$  for Br<sup>-</sup> are 0.02, 0.005, 0.01, and 0.005 (i.e., 20%,

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50%, 50%, and 50%, the remaining reacts with Cl<sup>-</sup>, see Table S3 in Sarwar et al. (2019)).

For the last three uptake coefficients, they are the same as those in Wang et al. (2021a). But the “effective”  $\gamma$  for Br<sup>-</sup> are smaller in Wang et al. (2021a) because only 15% of INO<sub>3</sub>, INO<sub>2</sub>, and HOI react with Br<sup>-</sup> and the other 85% react with Cl<sup>-</sup> (see R10–12 in Wang et al. (2021a)). Therefore, the debromination rate through RS1–RS4 should be higher. However, since “[m]ost of the SSA debromination in the model is from Reaction (R1)” (Zhu et al. 2019) (R1 is RS1 here), the most important parameter is  $\gamma$  of HOBr.

In our model, the uptake of HOBr is simply treated like INO<sub>3</sub>, INO<sub>2</sub>, and HOI. However, in the studies of Zhu et al. (2019) and Wang et al. (2021a), more complicated treatment of the uptake of HOBr is implemented. First, HOBr can react with dissolved SO<sub>2</sub> in addition to Cl<sup>-</sup> and Br<sup>-</sup>. Second,  $\gamma$  of HOBr is a function of ion concentrations and pH, instead of a constant. Third, much more HOBr reacts with Br than Cl (9:1 when Br/Cl > 5 × 10<sup>-4</sup> which is the case in our simulations in the whole domain, instead of 2:8).

It is not clear what values of  $\gamma$  of HOBr are as a function of ion concentrations and pH. Previous GEOS-Chem studies used constant  $\gamma$ , but both 0.1 and 0.2 were used (Fernandez et al. 2014; Ordóñez et al. 2012; Parrella et al. 2012). Our model follows that of Fernandez et al. (2014), taking  $\gamma=0.1$ . Updating  $\gamma$  as a function of ion concentrations, Schmidt et al. (2016) showed larger Br<sub>y</sub> source from debromination than that of Parrella et al. (2012) (1620 > 1420 GgBr/yr). Then, we may infer that the variable  $\gamma$  has a larger annual average than the constant 0.2 in Parrella et al. (2012). The resulting higher BrO leads to the exclusion of debromination of SSA in some GEOS-Chem studies (e.g., Sherwen et al. 2016b; Stone et al. 2018), which in turn results in the inclusion of the reaction SO<sub>2</sub>+HOBr that is intended to consume HOBr (compete with HOBr+Br<sup>-</sup>). The net result of these two opposite updates (increase HOBr uptake but decrease Br<sub>2</sub> release) of GEOS-Chem model is unclear, and we simply assume it is null (i.e., the increase and decrease cancel out each other in terms of Br activation). Then in previous GEOS-Chem studies  $\gamma$  of HOBr for Br<sup>-</sup> and Cl<sup>-</sup> is usually 0.2 as in Parrella et al. (2012). From this consideration, the model in our study probably underestimates debromination rate by 50%. Furthermore, the yield of BR<sub>2</sub> is significantly underestimated compared to those studies, resulting a further underestimation of debromination rate.

However, the exclusion of debromination of SSA in several previous GEOS-Chem studies (Schmidt et al. 2016; Sherwen et al. 2016b; Stone et al. 2018) but without decreasing BrO burden (Zhu et al. 2019) indicates that there are more complicated interactions between different reactive bromine species (Br<sub>y</sub>). Since Br chemistry influences OH mainly through consuming O<sub>3</sub> (Stone et al. 2018) which will produce BrO (and BrO is mainly produced from Br+O<sub>3</sub>), constraining modelled BrO is enough for our purpose in this study. Since there are very few

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measurements in the Western Pacific, the constrain in our study is inadequate. But more measurements are needed for further improvement of modelling.

Because the story of the development of debromination from SSA in previous GEOS-Chem study is very complicated, we only briefly mention it in our revised manuscript:

Recent model GEOS-Chem studies improved the uptake of HOBr substantially, but the two major revisions have opposite effects on BrO: increasing HOBr uptake by using more sophisticated parameterizations (Schmidt et al. 2016) and decreasing Br<sub>2</sub> yield by adding competition reactions of HOBr with S(IV) (Chen et al. 2017; Wang et al. 2021b; Zhu et al. 2019). The uptake of HOBr in our study is simply parameterized with a constant reactive uptake coefficient 0.1 (Sarwar et al. 2019), which may result in a lower debromination rate. However, since Br chemistry influences OH mainly through the consumption of O<sub>3</sub> (Stone et al. 2018), the constraining on modelled BrO is sufficient for our purpose. as shown in 3.1, modelled BrO is comparable to previous studies (Zhu et al. 2019), indicating the update of HOBr chemistry may not be critical to our results, but more measurements of BrO with seasonality information are needed for further evaluation of the impacts of Br chemistry. (Line 598-609)

**21. Line 400. Indeed, the uptake of HOI onto the sea salt particles could significantly alter the fate of HO<sub>2</sub> and then OH (i.e. HO<sub>2</sub> + Y term) and most of the results in this study. This was previously studied by Kanaya et al. GRL 2002 in the Asian domain.**

**Response:**

Our chemical mechanism includes the HOI uptake and the uptake coefficient, 0.01, is similar to previous studies (e.g., 0.01 in Sherwen et al. (2016a), which is according to the compile of Sander et al. (2011)). Kanaya et al. (2002) tested higher uptake coefficient (0.1 and 0.5), but the IO concentration used there are too high (12–25 pptv) and there is no inorganic iodine emission, limiting the generalization of their results. Nevertheless, it is possible that HOI uptake coefficient is higher than currently known and the influence could be large. We add more discussions in the section 3.5 Limitations as follows:

A recent observation study reported a much faster uptake of HOI and release of ICl and IBr (Tham et al. 2021), which may have large impacts on the cycling of HOI. In particular, since the photolysis of ICl and IBr is faster than that of HOI, iodine atom would be more rapidly recycled and O<sub>3</sub> would be more efficiently consumed (Tham et al. 2021) but without producing OH (similar to reactions RS1 and RS2). At the same time, OH production from HOI photolysis would be slower since HOI is more efficiently removed from the system. As a result, the impact of iodine chemistry on OH would be more negative (Kanaya et al. 2002).

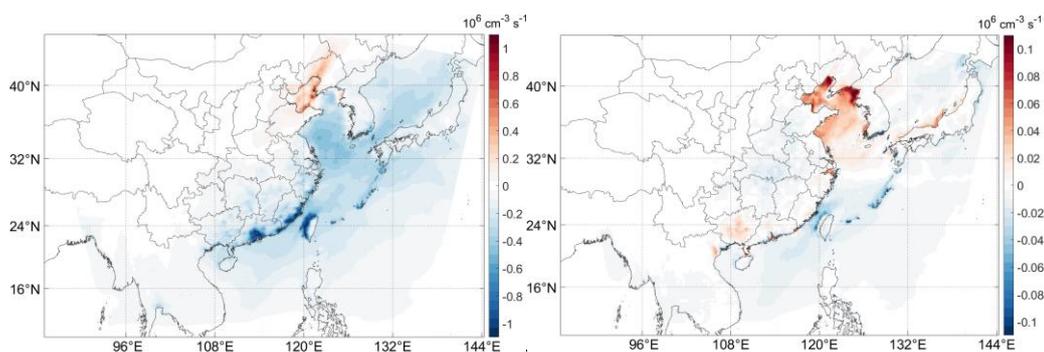
**22. Line 409. There are a series of laboratory studies examining uptake of HO<sub>2</sub> onto**

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*sea-spray aerosol particles (Taketani et al., 2008, 2009).*

**Response:**

We conduct sensitivity simulations to evaluate the impact of HO<sub>2</sub> uptake under the influence of marine halogen chemistry. Surprisingly, the uptake of HO<sub>2</sub> does not significantly change the impact of SSA emission on the OH production as shown in Fig. R5 that with or without HO<sub>2</sub> uptake have limited impact on the SSA-induced  $\Delta P_{OH}$ . Therefore, we delete relevant discussion in section 3.5.



**Fig. R5.** Change of  $P_{OH}$  caused by SSA emission with HO<sub>2</sub> uptake (left, see also Fig. 4a for that without HO<sub>2</sub> uptake in the main text) and the difference between that with and without HO<sub>2</sub> uptake (right). Note the different scales.

**23. Line 413. What is the "mass interaction"?**

**Response:**

Sorry for the confusion. We missed some word. We modify it to “[impacts of gas/particle exchange](#)”.

**24. Throughout the manuscript: Was all  $P(OH)$  studied always at the lowest model layer? How will the results change, when studying the whole atmospheric boundary layer?**

**Response:**

Yes. We focused on the surface layer in this MS. The results could get some changes in the PBL. For example, the different timescales of the positive and negative effect of iodine chemistry (positive from local HOI cycling, negative from O<sub>3</sub> consumption which can be accumulated) would lead to a more negative impact of iodine chemistry on  $P_{OH}$  in higher layer over the ocean because decreased O<sub>3</sub> can be accumulated but HOI cycling is more active only in the lower layer near to the iodine source. Due to the length of our manuscript, we do not discuss further in our revised manuscript.

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