

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-876

Anonymous Referee #1

Referee comment on "The impacts of marine-emitted halogens on OH radicals in East Asia during summer" by Shidong Fan and Ying Li, Atmos. Chem. Phys. Discuss.,
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This manuscript, entitled "The impacts of marine-emitted halogens on OH radical in East Asia during summer", by Shidong Fan and Ying Li, presents a modeling study using WRF-CMAQ, a community model implemented with tropospheric halogen chemistry with a focus on marine emissions of several key reactive halogen compounds. The iodine chemical mechanism appears to be fairly comprehensive. By using process analysis tools (integrated reaction rate and integrated process rate) and several sensitivity tests, the authors show that the reactive iodine chemistry have major impacts on the production of OH radicals in the marine boundary layer in East Asia. The sensitivity tests are nicely designed such that the impacts of various processes can be separated in a logical manner. The conclusions are of interest to the broad community and several research gaps for future investigation are identified. The paper is generally well organized and structured, although the clarity and logic could use some improvement. However, a few key science questions are not clearly elucidated, which are elaborated in the Major Comments section. I also have several Minor and Technical comments. All these comments and suggestions are intended to strengthen the manuscript and to improve the clarity. I recommend this manuscript for publication after Major Revision.

Major comments/suggestions:

The main results (Figure 2 and Figure 3) are very interesting. Yet, some of the discussion presented in the current version of the manuscript is vague and fails to address two key questions:

(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.

(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 I₂ 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.

Specific comments:

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

Line 33: This is a vague description. HO₂ → OH is not always a net source of OH, since a major fraction of HO₂ is actually produced from OH. Please rewrite this sentence: either tease out the primary fraction of HO₂ (e.g., from formaldehyde) or discuss the sum of OH and HO₂. After all the interconversion between OH and HO₂ is fast.

Line 37: ... under low-NO_x condition. Also please clarify what exactly is "low-NO_x condition". Is this referring to the condition when RO₂ fate is dictated by non-NO_x pathways? If this is the case, often the NO_x threshold can be very low.

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

Line 46: ... under high NO_x condition.

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_x 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_x and they use box model with ozone unconstrained.

Line 45: "One relevant reaction is that XO (X=Cl, Br, and I) transform HO₂ 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).

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 HO_x is that both OH and HO₂ are reduced by 3-4%. This is buffered by many other processes but the primary driver is a global ~10% decrease in HO_x production from ozone. This is qualitatively consistent with previous studies.

Line 56-57: "For example, the conversion of HO₂ to OH enhanced by XO would consume HO₂, which in turn should decrease the conversion through HO₂+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.

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.

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.

Line 65-66: This is very vague as written. Do the authors refer to the reactive halogens (e.g., I₂/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 I₂/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).

Line 135-136: please show the original and scaled halocarbon emissions. Please note that although this is a widely used 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)

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).

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.

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.

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

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.

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.

Lines 197-198: What is this "middle area of the ocean"?

Line 236, 240: photolysis of O₃: note that the photolysis of O₃ is not really producing OH directly, it is the produced O₁D reaction with water vapor that generates OH. Please clarify how this P_OH_O1D term is calculated.

Line 252: "Since HOX is a primary source of OH..." I do not think HOX should be considered as a primary source of OH. Essentially what it does is converting HO₂ to OH:

$X + O_3 = XO + O_2$
 $XO + HO_2 = HOX + O_2$
 $HOX + hv = X + OH$
Net: $O_3 + HO_2 = OH + 2*O_2$

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 $HO_2 + NO/O_3/...$, 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.

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.

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.

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

Line 314-: Sure Cl itself is a strong oxidant but why would Cl oxidation affect OH radical production? Is it thru $RO_2 \rightarrow HO_2 \rightarrow OH$ channel? Please clarify.

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.

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