The impacts of marine-emitted halogens on OH radical in East Asia during summer

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S1. Details about the iodine chemistry

In the catalytical consumption of O_3 through R1–R3, consumption of one O_3 would produce one OH radical and P_{OH} concentration would increase because most products of O_3 photolysis are O^3P instead of O^1D and only a small part of O^1D will react with H_2O to form OH (Seinfeld and Pandis, 2016). Indeed, the OH production through chemical reactions is generally increased (Fig. 6d). However, there are other pathways cycling iodine than R1–R3 that can catalyze R1 but not R3. For example, the photolysis of iodine oxides is generally more important than the photolysis of HOI (Saiz-Lopez and von Glasow, 2012;Tham et al., 2021).

$$IO + IO \rightarrow OIO + I \tag{RS1}$$

$$OIO + h\nu \rightarrow I + O_2 \tag{RS2}$$

These pathways, which are more important than R3 in high-XO conditions (Saiz-Lopez and von Glasow, 2012), can cycle iodine atom (and destroy O_3) without producing OH, resulting in a decrease of OH. If these pathways are much stronger than the cycling of R1–R3, the lower efficiency of R1 might be compensated because R1 would be much faster than R3 and chemical ΔP_{OH} could be negative. However, the negative ΔP_{OH} in the Philippine Sea is not caused by the stronger other pathways cycling iodine because the relative strength of these pathways compared to R3 does not show a maximum in the area (Fig. S8c). Therefore, it is not the competition between R1 and R3, that results in the higher decrease of P_{OH_O1D} than the increase of P_{OH_HOX} in the Philippine Sea.

The competition between pathway 1 (P_{OH_O1D}) and 3 (P_{OH_HOX}) in changing P_{OH} has three parts because there are three steps from R1 to ΔP_{OH_O1D} (while P_{OH_HOX} is almost just the rate of R3): O_3 destruction by iodine, change of O_3 concentration, and OH formation from O_3 photolysis. The first is just discussed above. For the third, the integrated reaction constant from O_3 to OH, denoted as $k_{OHfrO_3} := \frac{2\times k_{O1D+H2O}[H_2O]\times J(O^1D)}{k_{O1D+M}[M]+k_{O1D+H2O}[H_2O]} = \frac{P_{OH\_O1D}}{[O_3]}$, has significant north-south difference due to the longitudinal distribution of actinic flux, but in the area with negative ΔP_{OH} there is no maximum and in the maximum area there is no negative ΔP_{OH} (Fig. S8f). Therefore, k_{OHfrO_3} is unlikely to be responsible for the larger decrease of P_{OH_O1D} east to the Taiwan island.

The remaining one is the change of O_3 concentration. The pattern of ΔO_3_daytime has obvious difference with that of ΔP_{I_HOI}, especially in the Sea of Japan, the Yellow Sea, the areas east to Vietnam, and west part of the Philippine Sea (Figs. S8b,d). Using ΔO_3_daytime/ΔP_{Ieff} (effective production rate of iodine, $=P_I-P_{I\_IO}-P_{I\_withNO2}$) to represent the response of O_3 concentration to the O_3 consumption rate by iodine, we can see in Fig. S8e that the maxima of this response appear exactly in the area with negative iodine-chemistry-induced ΔP_{OH} in the Philippine Sea. Hence, it is the mismatch of changes of O_3 concentration and O_3 loss rate that leads to the negative iodine-chemistry-induced ΔP_{OH} in the Philippine Sea. The mismatch of the patterns of ΔO_3_daytime and the loss rate of O_3 (≈production rate of iodine atom) is probably caused by the transport processes of O_3 because in the Philippine Sea O_3 concentration is strongly correlated with wind speed (Fig. S9), indicating a strong contribution of transport to O_3. The area with negative ΔP_{OH} is in the downwind of the Philippines. Therefore, the chemical loss of O_3 in the Philippines may remotely decrease the O_3 concentration in this area.

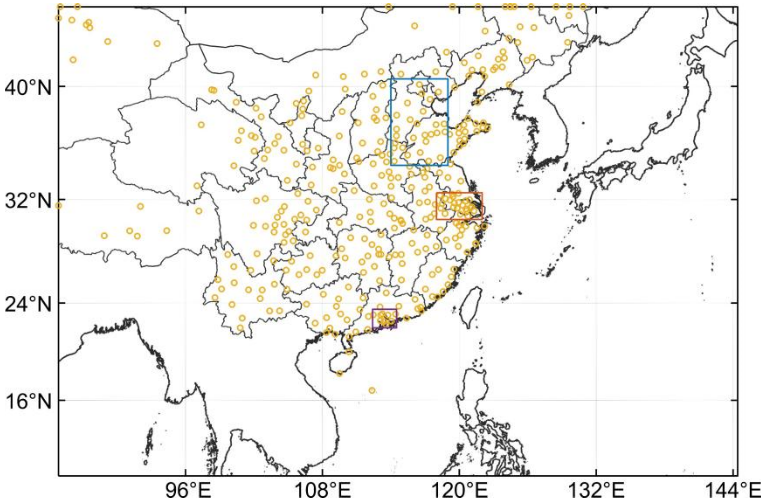

Figure S1. Positions of the observation stations for model evaluation. The yellow circles are stations. The blue, orange, and violet boxes indicate the NCP, YRD, and PRD areas, respectively.

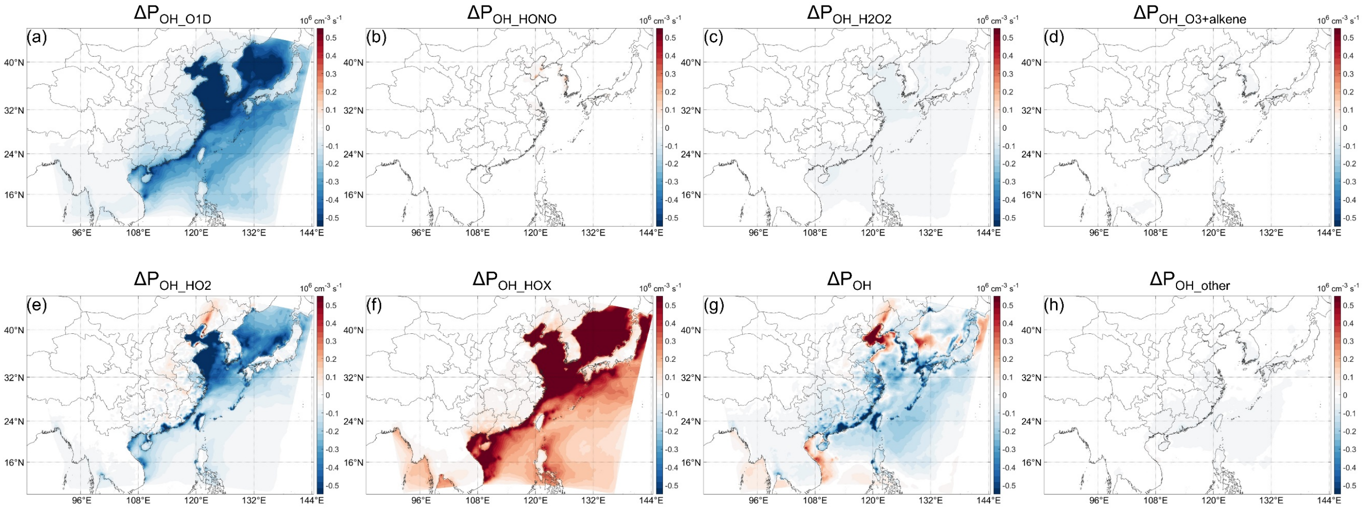

Figure S2. The same as Figure 3 but for All_low case.

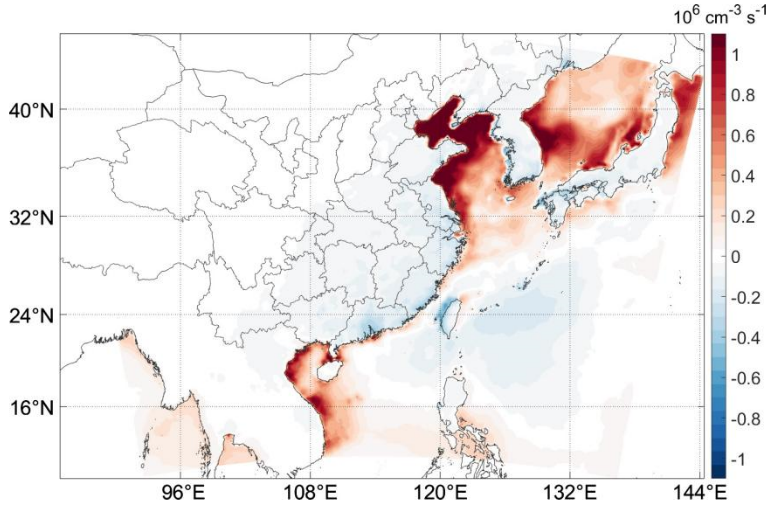

Figure S3. Change of P_{OH} through pathway 1 (ΔP_{OH_O1D}) and 3 (ΔP_{OH_HOX}) in All_high case compared to BASE case.

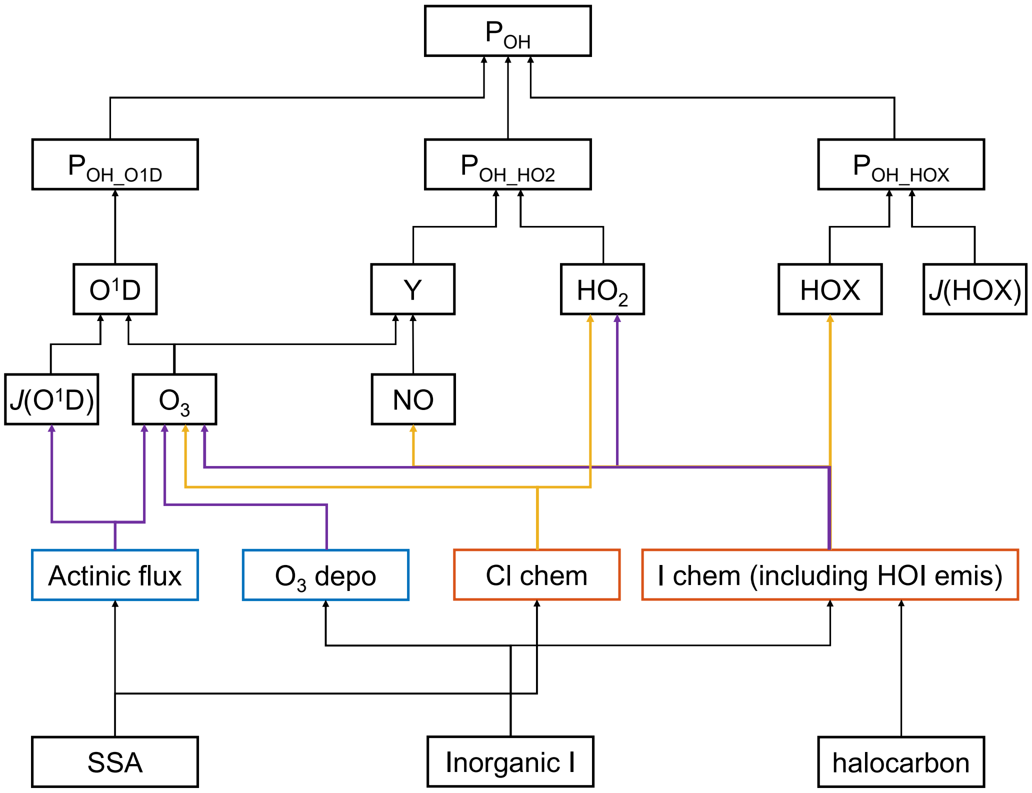

Figure S4. Schematic representation of the three main pathways that halogen species influence OH production (P_{OH_O1D}, P_{OH_HO2}, and P_{OH_HOX}) and their main controlling factors. The boxes in blue and orange represent independent and interrelated (chemical) factors, respectively. The purple and yellow arrows represent decrease and increase of the target species or parameters, respectively.

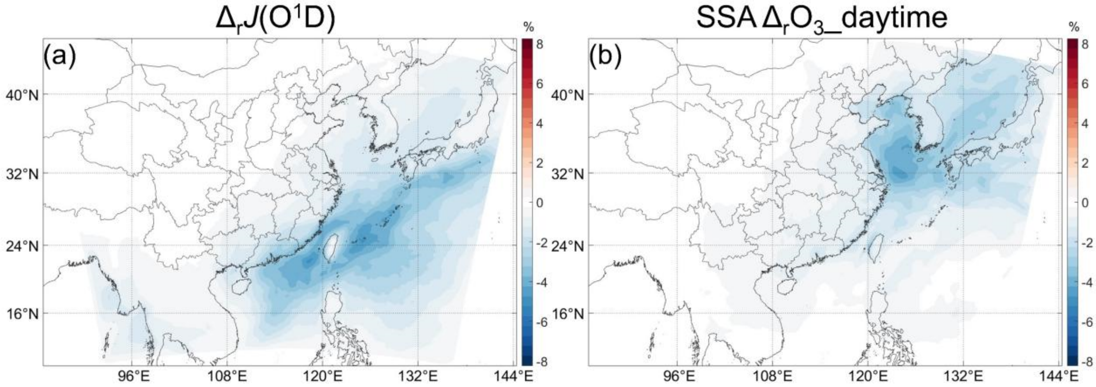

Figure S5. Relative change of (a) $J(O^1D)$ and (b) daytime O_3 caused by the extinction effect of SSA, approximated by $\Delta_r O_3$_daytime in SSA_Cl without the uptake of N_2O_5 and yield of $ClNO_2$.

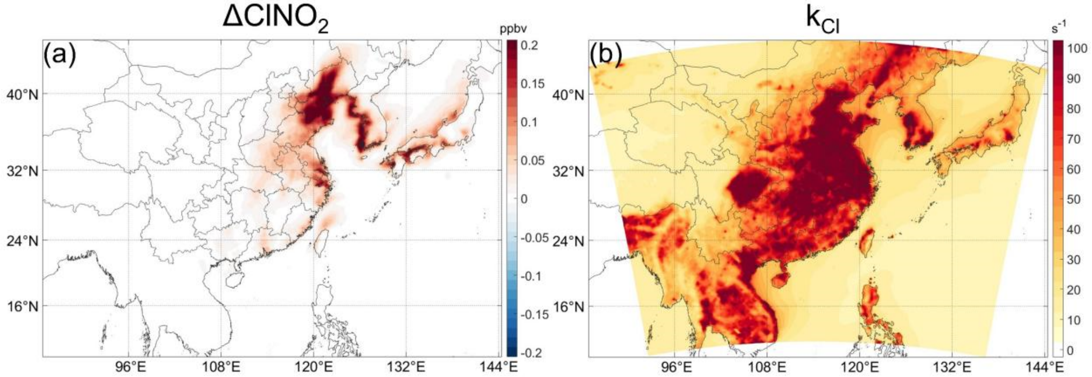

Fig. S6. (a) $ClNO_2$ change in SSA_Cl case compared to BASE case. (b) k_{Cl} in BASE case (Δk_{Cl} is very small).

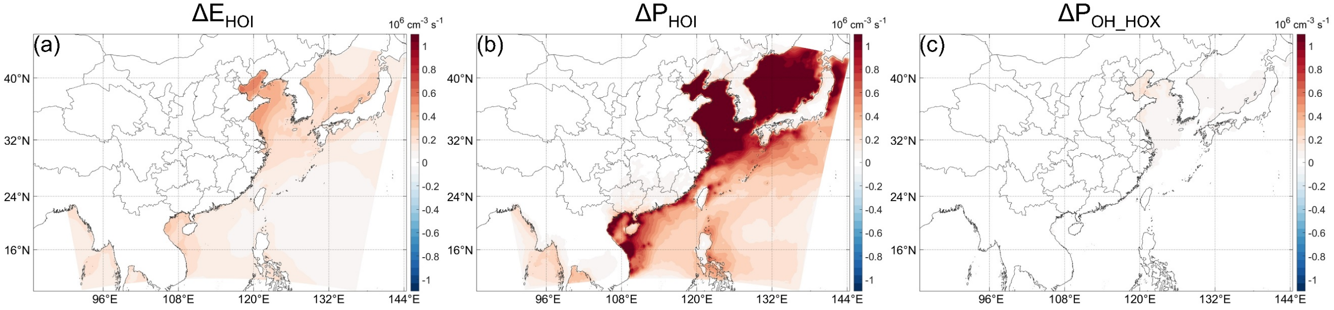

Figure S7. Change of HOI (a) emission rate and (b) production rate from HO_2+IO in All_high case compared to BASE case. (c) Change of P_{OH_HOX} by replacing HOI emission with an equivalent amount of I_2 in All_high case, approximating the contribution of direct HOI emission to P_{OH_HOX}.

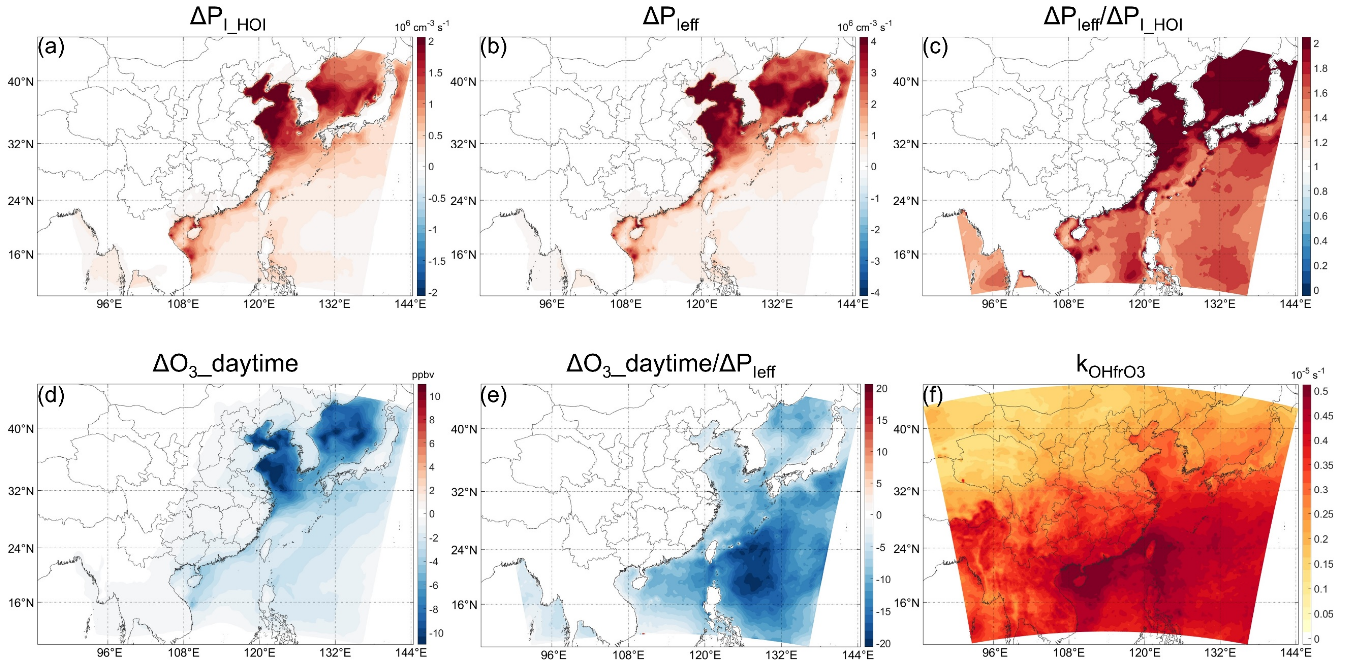

Fig S8. (a) Iodine atom production rate from HOI (ΔP_{I_HOI}) and (b) from effective reactions (ΔP_{Ieff}, iodine atom that can consumes O_3, i.e., excluding IO photolysis which will produce O and reactions which produce NO_2). (c) The ratio between (b) and (a), representing the relative strength of (b) compared to (a). (d) Daytime (LT 8:00–16:00) O_3 decrease. (e) The ratio between (d) and (b), representing the response of (d) to (b). (f) Integrated reaction constant from O_3 to OH (including O_3 photolysis and O^1D+H_2O reaction, see SI). Δ represents InorgI_chem−BASE case, representing the contribution from atmospheric iodine chemistry. (f) is for BASE case.

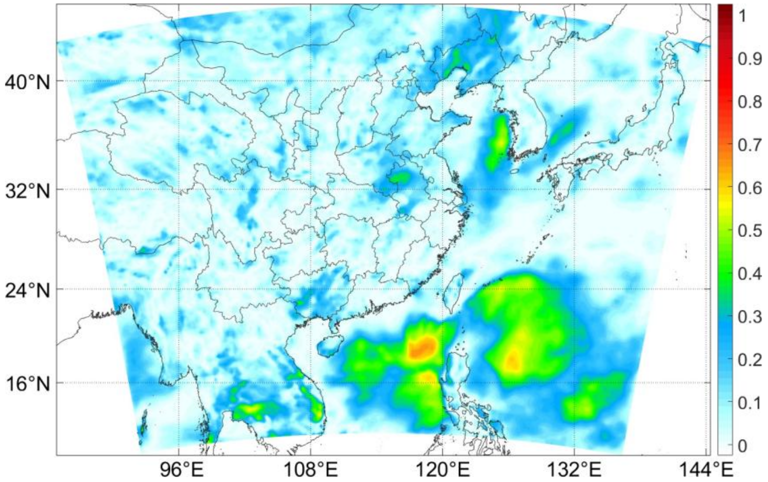

Fig. S9. Squares of the correlation coefficients between O_3 concentration and 10 meter wind speed in the InorgI_chem case.

References

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