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$_3$P instead of O$_1D$ and only a small part of O$_1D$ will react with H$_2$O 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).

\[
\text{IO} + \text{IO} \rightarrow \text{OIO} + \text{I} \quad (RS1)
\]

\[
\text{OIO} + h\nu \rightarrow \text{I} + \text{O}_2 \quad (RS2)
\]

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 $\Delta P_{OH}$ could be negative. However, the negative $\Delta P_{OH}$ 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 $\Delta P_{OH,O1D}$ (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 $k_{OHfrO3}$, has significant north-south difference due to the longitudinal distribution of actinic flux, but in the area with negative $\Delta P_{OH}$ there is no maximum and in the maximum area there is no negative $\Delta P_{OH}$ (Fig. S8f).

Therefore, $k_{OHfrO3}$ 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 $\Delta$O$_3$$_{\text{daytime}}$ has obvious difference with that of $\Delta$P$_{\text{I, HOI}}$, especially in the Sea of Japan, the Yellow Sea, the areas east to Vietnam, and west part of the Philippine Sea (Figs. S8b,d). Using $\Delta$O$_3$$_{\text{daytime}}$/\Delta$P$_{\text{eff}}$ (effective production rate of iodine, $=P_\text{I} - P_{\text{I, IO}} - P_{\text{I, with NO2}}$) 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 $\Delta$P$_{\text{OH}}$ 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 $\Delta$P$_{\text{OH}}$ in the Philippine Sea. The mismatch of the patterns of $\Delta$O$_3$$_{\text{daytime}}$ and the loss rate of O$_3$ ($\approx$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 $\Delta$P$_{\text{OH}}$ 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 ($\Delta P_{OH, O1D}$) and 3 ($\Delta P_{OH, HOX}$) 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 $\Delta O_3 \_\text{daytime}$ 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 ($\Delta k_{Cl}$ 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 ($\Delta P_{I\text{-HOI}}$) and (b) from effective reactions ($\Delta P_{I\text{eff}}$, 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$^1$D+H$_2$O reaction, see SI). $\Delta$ represents InorgI$_\text{chem}$–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$_\text{chem}$ case.
References