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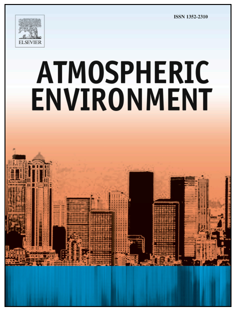

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Influence of bromine and iodine chemistry on annual, seasonal, diurnal, and background ozone: CMAQ simulations over the Northern Hemisphere

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ABSTRACT

Bromine and iodine chemistry has been updated in the Community Multiscale Air Quality (CMAQ) model to better capture the influence of natural emissions from the oceans on ozone concentrations. Annual simulations were performed using the hemispheric CMAQ model without and with bromine and iodine chemistry. Model results over the Northern Hemisphere show that including bromine and iodine chemistry in CMAQ not only reduces ozone concentrations within the marine boundary layer but also aloft and inland. Bromine and iodine chemistry reduces annual mean surface ozone over seawater by 25%, with lesser ozone reductions over land. The bromine and iodine chemistry decreases ozone concentration without changing the diurnal profile and is active throughout the year. However, it does not have a strong seasonal influence on ozone over the Northern Hemisphere. Model performance of CMAQ is improved by the bromine and iodine chemistry when compared to observations, especially at coastal sites and over seawater. Relative to bromine, iodine chemistry is approximately four times more effective in reducing ozone over seawater over the Northern Hemisphere (on an annual basis). Model results suggest that the chemistry modulates intercontinental transport and lowers the background ozone imported to the United States.

Keywords: bromine, iodine, ozone, background ozone, CMAQ

1.0 INTRODUCTION

Although anthropogenic emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOC) within the United States (U.S.) have a large influence on ambient surface ozone (O_3) concentrations, other processes such as natural emissions, stratospheric intrusions, and long-range transport can affect surface O_3 concentrations at some locations within the U.S. Among these natural emissions are chemical compounds from the ocean surface that can reduce atmospheric O_3 concentrations through catalytic reactions. Bromine reactions deplete O_3 in the tropical marine boundary layer (Dickerson et al., 1999) and when combined with iodine reactions, they can deplete O_3 much faster than would have been expected if they acted individually (Saiz-Lopez et al., 2007; Mahajan et al., 2010). Bromine and iodine are produced in the ocean through both biotic and abiotic pathways resulting in measurable concentrations of both organic and inorganic species within the marine boundary layer. Several modeling studies have implemented marine bromine and iodine emission sources and chemistry with increasing levels of scope, ranging from one-dimensional models (e.g. von Glasow, et al., 2002a; von Glasow, et al., 2002b) to global chemical transport models (e.g. Ordóñez, et al., 2012; Saiz-Lopez et al., 2012; Saiz-Lopez et al., 2014; Fernandez et al., 2014; Sherwen et al., 2016a; Sherwen et al., 2016b).

A disconnect between anthropogenic precursor emissions and surface O_3 concentrations at some U.S. sites has led to an increased focus on background O_3 (Fiore et al., 2002; Fiore et al., 2003; Fiore et al., 2014). The U.S. Environmental Protection Agency (EPA) considers background O_3 to be any O_3 formed from sources or processes other than U.S. manmade emissions of NO_x, VOC, methane, and carbon monoxide (EPA, 2016). Previous photochemical modeling studies

(Parrish et al., 2009; Cooper et al., 2010; Zhang et al., 2011; McDonald-Buller et al., 2011) which estimated the contribution of background sources on U.S. O_3 concentrations have found that (1) seasonal mean background concentrations are highest in the Intermountain West, (2) seasonal mean background concentrations are generally highest in the Spring and early Summer, (3) background impacts can occur on episodic and non-episodic scales, and (4) air quality models are not capable of estimating background values accurately on a daily basis.

Background O_3 levels in coastal areas are affected by marine boundary layer chemistry, which is influenced by atmosphere-ocean interactions. Several previous studies examined the impacts on O_3 by bromine (e.g. Ordóñez, et al., 2012; Fernandez et al., 2014; Yang et al., 2005; Parrella et al., 2012; Schmidt et al., 2016; Breton et al. 2017) and iodine chemistry (e.g. Saiz-Lopez et al., 2014; Sherwen et al., 2016a; Sherwen et al., 2016b; McFiggans et al., 2000; Long et al., 2014; Badia et al., 2017) using air quality models. Sarwar et al. (2015), Gantt et al. (2017), and Muñiz-Unamunzaga et al. (2018) showed that including marine bromine and iodine chemistry in the Community Multiscale Air Quality (CMAQ) model not only reduces summertime marine boundary layer O_3 concentrations by more than 5 ppbv, but also reduces O_3 in the free troposphere and inland areas far from the coast. In this study, we refine the marine bromine and iodine chemistry in the CMAQ model and extend the simulations to examine its influence on annual, seasonal, diurnal, and background O_3.

2.0 METHODOLOGY

CMAQ is a 3-D chemical transport model containing comprehensive treatments of many important atmospheric processes and is widely used for both regulatory and research purposes (e.g. Appel et al., 2013; Appel et al., 2017; Ring et al., 2018; Qiao et al., 2018). We use the hemispheric version (Mathur et al., 2017) of CMAQ version 5.2 (www.epa.gov/cmaq) to simulate the year 2006 with meteorological fields generated from the Weather Research and Forecasting (WRFv3.8.1) model employing the Thompson microphysics option (Skamarock et al., 2008). WRF results were further processed using the Meteorology Chemistry Interface Processor (Otte and Pleim, 2010) (MCIPv4.3) to prepare CMAQ-ready meteorological files. The model vertical extent reaches to 50 hPa containing 44 layers of varying thickness and uses 108-km horizontal grid spacings. The surface layer has a thickness of 20 meters.

The 2005 Carbon Bond chemical mechanism (CB05e51) containing updated toluene, oxidized nitrogen, and isoprene reactions (Appel et al., 2017) is combined with the chlorine (Sarwar et al., 2012), bromine, and iodine chemistry for this study. Sarwar et al. (2015) incorporated an initial version of bromine and iodine chemistry into CMAQ and examined its lower and upper limits of the impacts on O_3. The upper limit included photolysis of higher iodine oxides while the lower limit did not. The model without the photolysis of iodine oxides yielded lesser reduction of O_3 over seawater (15%) compared to the model with the photolysis of iodine oxides which reduced O_3 by 48%. Since this 48% reduction resulted in unrealistically low O_3 concentrations in Sarwar et al. (2015), photolysis rates of higher iodine oxides have not been included in any publicly available version of the CMAQ model. Sarwar et al. (2015) also included one heterogeneous reaction of bromine nitrate.

In this study, the CMAQ bromine and iodine chemistry described in Sarwar et al. (2015) is further improved to include photolysis of higher iodine oxides (Table S1-S2), several heterogeneous reactions of bromine and iodine species (Table S3) with aerosol chloride (Cl^-) and bromide (Br^-), and refined bromine and halocarbon emissions. In the previous CMAQ model, photolysis rates of higher iodine oxides were calculated using absorption cross-section and quantum yield from Saiz-Lopez et al. (2014). Sherwen et al. (2016a) used absorption cross-section and quantum yield of iodine nitrate for calculating photolysis rates of higher iodine oxides which is now used in the CMAQ model.

We also incorporate several aqueous-phase reactions of bromine species following Long et al. (2013) (Table S4). Cloud chemistry of bromine species was added to the CMAQ cloud module "AQCHEM-KMT" (Fahey et al. 2017) using the Kinetic PreProcessor (KPP) v.2.2.3 (Damian et al. 2002). AQCHEM-KMT simulates the evolution of species in and around cloud water by calculating kinetic mass transfer between gas and aqueous phases, interstitial aerosol scavenging, dissociation of ionic species, aqueous phase chemical reactions, and wet deposition.

Sarwar et al. (2015) used halocarbon, inorganic bromine, and inorganic iodine emissions in the CMAQ model, the rates of which are refined in this study. For halocarbon species, the emission rates are calculated following the procedures of Ordóñez et al. (2012) and Yarwood et al. (2012):

$$E_{HC} = E_{base} \times (O_F+S_F) \times A_{GC} \times f_{HC} \times f_{DP} \times \text{chl-}a \qquad (1)$$

where, E_{HC} is the halocarbon emission rates (moles s^{-1}), E_{base} represents the halocarbon base emission rate (moles s^{-1}), O_F is the open ocean fraction of a grid cell, S_F is the surf zone fraction of a grid cell, A_{GC} is the grid cell area (m^2), f_{HC} is a species-dependent emission factor, f_{DP} is a diurnal profile factor, and chl-*a* is the monthly climatological chlorophyll value (mg m^{-3}) from the Moderate Resolution Imaging Spectroradiometer (MODIS).

In Sarwar et al. (2015), chl-*a* values were capped at 1.0 following Yarwood et al. (2012); in this study, we used the actual chl-*a* values from MODIS which can be greater than 1.0 in coastal areas. This change in chl-*a* values necessitated a revision in the base emission rate from 1.2×10^{-11} in Sarwar et al. (2015) to 6.9×10^{-12} to replicate the global estimates of halocarbon emissions reported by Ordóñez et al. (2012). This revision was done outside the CMAQ framework by using the native MODIS derived global land/ocean grid areas and chl-*a* values. We iterated the base emission rate until suitable agreement with the Ordóñez et al. (2012) estimates was reached. The use of the revised base emission rate and the actual chl-*a* values reduces the total hemispheric halocarbon emissions estimates by ~20% compared to the estimates of Sarwar et al. (2015). It also changes the allocation of halocarbon emissions to different grid-cells. More halocarbon emissions are now allocated to coastal areas and less are allocated to open oceans compared to the estimates of Sarwar et al. (2015).

Refinement of the inorganic emissions included the replacement of the simplified treatment of directly emitting inorganic bromine emissions (Yang et al., 2005 and Sarwar et al., 2015) with the physically-based heterogeneous chemistry of bromine and iodine species (Table S3) following Fernandez et al. (2014) and Sherwen et al. (2016b). This required a revision to the sea spray emissions in CMAQ (Gantt et al., 2015) to include Br^- in the chemical speciation. Specifically, the sea spray emissions are speciated by mass (gm/gm) following Millero (1996): Cl^- = 0.5528, Na^+ = 0.3080, SO_4^{2-} = 0.0775, Ca^{2+} = 0.0118, Mg^{2+} = 0.0367, K^+ = 0.0113, and Br^- = 0.0019. We also updated the minimum wind speed in the inorganic iodine emissions parameterization (McDonald et al., 2014) from 3 m s^{-1} in Sarwar et al. (2015) to 5 m s^{-1} following the value used for the GEOS-Chem model (Sherwen et al., 2016a) which reduces the emissions estimates by ~15%. Hemispheric halocarbon and inorganic iodine emission rates, along with global estimates reported in previous studies, are shown in Table 1. Generally, our halocarbon emissions estimates for the Northern Hemisphere are lower than the reported global estimates while inorganic iodine emissions estimates fall between the reported ranges of global estimates.

Table 1: Halocarbon and inorganic iodine emissions estimates

Species	Hemispheric annual estimates in this study (Gg)	Global annual estimates from published studies (Gg)
$CHBr_3$	301	533
CH_2Br_2	51.5	67.3
CH_2BrCl	6.1	10.0
$CHBr_2Cl$	14.8	19.7
$CHBrCl_2$	14.5	22.6
CH_3I	135	303
CH_2ICl	148	234
CH_2IBr	54.4	87.3
CH_2I_2	73	116
$HOI+ 2xI_2$	2052	1,900 – 3,230

Note: Global annual estimates of halocarbon emissions are taken from Ordóñez et al. (2012), global annual estimates of $HOI+2\times I_2$ are taken from Saiz-Lopez et al. (2014) and Sherwen et al. (2016a)

We performed six annual simulations for this study that can be grouped in three pairs. In the first pair, one simulation used CB05e51 along with the chlorine chemistry (hereto referred as “No_Br/I”), while the other added bromine and iodine chemistry (“Added_Br/I”). A second set of simulations was completed to investigate the influence of the bromine and iodine chemistry independently. In this second pair, one simulation added only bromine chemistry updates (“Added_Br”) while the other added only iodine chemistry updates (“Added_I”). The final set of simulations was completed to investigate the impact of bromine and iodine chemistry on background O_3 over the U.S. For the third pair, the model chemistry was identical to the first pair but with anthropogenic emission sources over North America were zeroed out ("No_Br/I_NoAnth" and "Added_Br/I_NoAnth", respectively). All the annual simulations were completed with a three-month spin-up period (October – December of 2005) and initialized from previous model results (Xing et al., 2016).

3.0 RESULTS AND DISCUSSSION

3.1 Predicted BrO (bromine monoxide) and IO (iodine monoxide)

BrO and IO are reaction products of the bromine and iodine chemistry. Annual mean daytime BrO and IO concentrations are shown in Figure 1. BrO concentrations of 0-0.8 pptv are predicted over large oceanic areas. However, higher values (>0.8 pptv) are also predicted over limited areas of mid-latitude oceans. In contrast, IO concentrations of 0-3.0 pptv are predicted over large oceanic areas and higher values (>3.0 pptv) are predicted only over limited oceanic areas. The current bromine/iodine chemistry enhances BrO and IO levels compared to the previous version of the chemistry without the photolysis of higher iodine oxides in CMAQ (Sarwar et al., 2015). For example, predicted summertime BrO levels with the previous version rarely exceed 0.5 pptv over the mid-latitude oceanic areas. In contrast, predicted BrO levels with the current version exceed 1.0 pptv over large portions of the mid-latitude oceanic areas. Overall, the current chemistry increases surface BrO levels by a factor of ~2.0 averaged over the entire seawater. Predicted summertime IO levels over most areas of seawater range from 0.5-1.5 pptv and 0.5-3.0 pptv for the previous and current versions of the chemistry, respectively. Overall, the current chemistry increases surface IO levels by a factor of ~1.5 averaged over the entire seawater. The BrO enhancement occurs primarily due to the inclusion of aqueous-phase and heterogeneous reactions while the IO enhancement occurs due to the inclusion of photolysis of higher iodine oxides and the heterogeneous reactions.

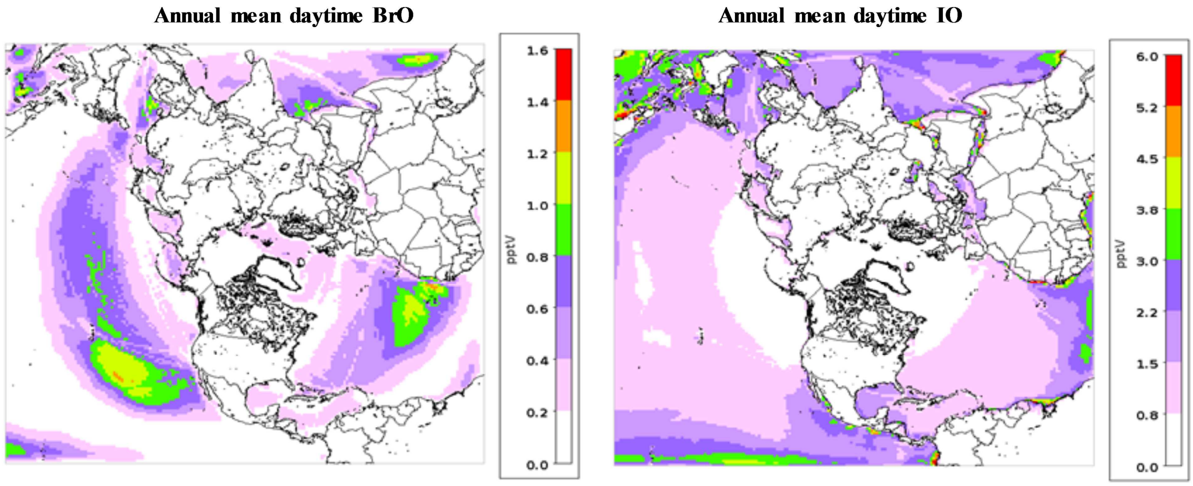

Figure 1. Simulated annual mean daytime surface BrO and IO concentrations with the bromine and iodine chemistry (Added_Br/I). Annual mean concentrations were multiplied by 2.0 to estimate approximate annual mean daytime BrO and IO concentrations.

We compare model predictions with published values from different years for an approximate evaluation of the bromine and iodine chemistry in CMAQ. Predicted BrO levels are lower than observed values at all locations (Table 2). CMAQ predicted values are also lower than ground-based daytime BrO measurements of <0.5-2.0 pptv and ship-based daytime BrO measurements of <~3.0-3.6 pptv (Saiz-Lopez et al., 2012). Thus, CMAQ generally under-predicts BrO levels. In contrast, CMAQ predicted values are similar to observed IO levels at Cape Verde Islands; Tenrife, Spain; Dagebüll, Germany but are lower than observed values at Brittany, France and Mace Head, Ireland (Table 2). Dix et al. (2013) measured IO concentrations over the Pacific Ocean in January of 2010 and reported an average value of 0.5 pptv inside the marine boundary layer. CMAQ predicted surface layer values range from 0.4 to 1.0 pptv over the region. Saiz-Lopez et al. (2012) reported that ground-based daytime IO measurements range from <0.2 to 2.4

pptv while ship-based daytime IO measurements range ~3.5 pptv. CMAQ predicted IO levels are similar to these reported observed values. Thus, CMAQ generally captures observed IO values.

Table 2: A comparison of observed daytime BrO and IO concentrations with CMAQ predictions

Location	Species	Observed value (pptv)	Predicted value (pptv)
Cape Verde Islands[a]	BrO	2.8	0.7
Dagebüll, Germany[b]	BrO	0.4	0.1
Brittany, France[b]	BrO	1.5	0.03
Mace Head, Ireland[c]	BrO	2.3	0.05
Cape Verde Islands[a]	IO	1.5	1.2
Dagebüll, Germany[b]	IO	0.7	0.8
Brittany, France[b]	IO	1.5	0.2
Mace Head, Ireland[d]	IO	1.2	0.14
Tenrife, Spain[d]	IO	1.2	1.1

Note: a - Mahajan et al., 2010; b – Peters et al., 2005; c – Saiz-Lopez et al., 2006; d – Allan et al., 2000. Cape Verde values represent daytime average of long-term measurements; CMAQ predicted annual daytime mean values are compared. Values at other locations represent daytime average over campaign; CMAQ predicted monthly daytime mean values are compared. Peters et al. (2005) reported average values for the entire campaign which we multiplied by 2.0 to estimate daytime average values.

3.2 Influence on annual mean O_3

Annual mean surface O_3 concentration over seawater without bromine and iodine chemistry is ~25 ppbv and increases with altitude (Figure 2). Consistent with the results of Sherwen et al., (2016b), the bromine and iodine chemistry reduces mean surface O_3 over seawater by 25% and reduces O_3 throughout the lower troposphere. Such reduction occurs due primarily to the reactions of O_3 with bromine and iodine radicals generated from photolysis and reactions of halocarbons and inorganic bromine and iodine species with hydroxyl radical. The influence of bromine and iodine chemistry on O_3 decreases with altitude and is negligible at ~15 km. Saiz-Lopez et al. (2014) and Sarwar et al. (2015) reported lower and upper limits (17-27% and 15-48%) of the impacts on O_3; and the O_3 changes reported in this study fall within their published ranges.

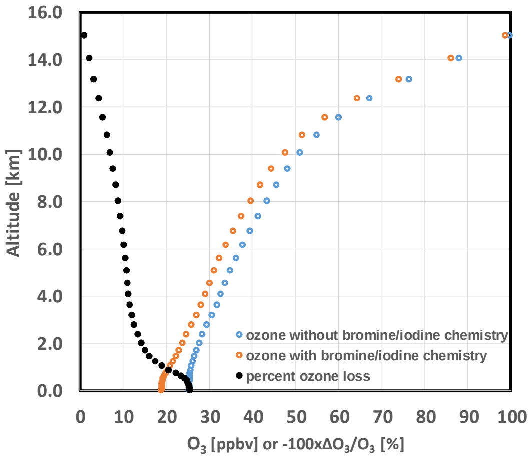

Figure 2. Simulated annual mean O_3 over seawater in the Northern Hemisphere without (No_Br/I) and with the bromine and iodine chemistry (Added_Br/I) and annual mean percent reduction of O_3 by the bromine and iodine chemistry [100 x (Added_Br/I - No_Br/I) / No_Br/I]

The spatial distribution of the annual mean O_3 without bromine and iodine chemistry is shown in Figure 3a with the highest values over portions of Asia, Africa, and the western U.S. and lower values predicted over seawater (especially over remote oceanic areas). The inclusion of bromine and iodine chemistry reduces surface O_3 by 3-12 ppbv over large areas of seawater (Figure 3b) and by 3-6 ppbv in many coastal areas including the Pacific, Gulf of Mexico, and Atlantic coasts. Its impact on O_3 over land is smaller than that over seawater, although all areas of the U.S. have a predicted ~2 ppbv or greater reduction in O_3 from the bromine and iodine chemistry.

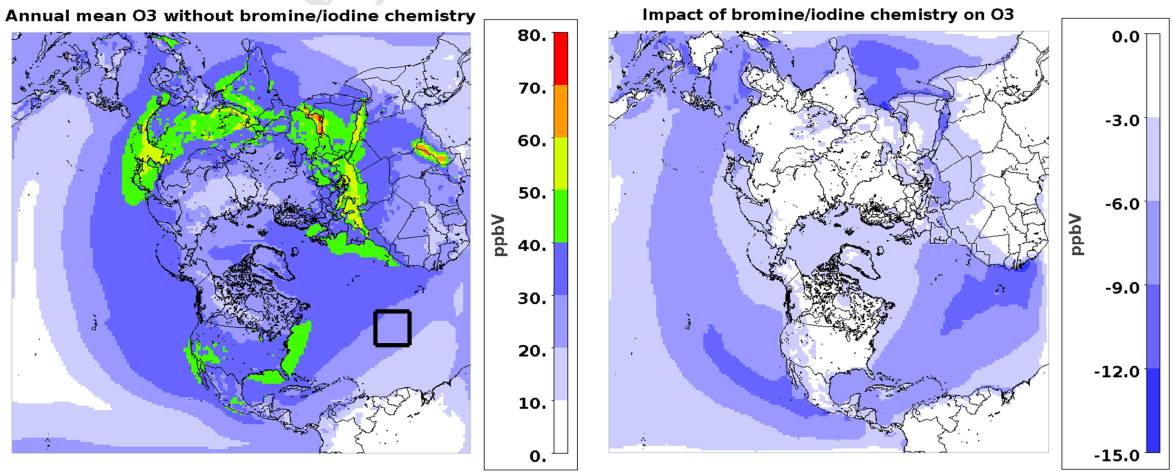

Figure 3. (a) Annual mean surface O_3 without the bromine and iodine chemistry (No_Br/I) (b) influence of the bromine and iodine chemistry on annual mean O_3 (Added_Br/I - No_Br/I). Black square box is the area over which diurnal, day-to-day, and monthly variations are calculated as shown in Figure 4 and 5.

The bromine and iodine chemistry in this study is more efficient in reducing O_3 over seawater compared to the previous version of the chemistry without the photolysis of higher iodine oxides in CMAQ (Sarwar et al., 2015). For example, the previous chemistry reduces summer-time O_3 over seawater generally by 2-8 ppbv while the current chemistry reduces O_3 over seawater by 3-12 ppbv. Both versions of the bromine and iodine chemistry have similar impacts over land areas.

3.3 Influence on diurnal variation of O_3

To examine the influence of the bromine and iodine chemistry on the diurnal variation of O_3, we calculated a mean diurnal profile for an area over the Atlantic Ocean (see Figure 3a) by averaging across all days in the annual simulation for each hour of the day, as shown in Figure 4a. The area is selected to minimize the influence of anthropogenic emissions on O_3. Predicted O_3 levels with the bromine and iodine chemistry are lower (by 7-8 ppbv) than those in simulations without the bromine and iodine chemistry. There is a pronounced diurnal cycle in both simulations, as O_3 concentrations increase from midnight and peak in the morning, then decrease to a minimum value in the afternoon before increasing again. This diurnal variation results from low concentrations of O_3 precursors over remote areas of seawater that limit O_3 production as has been previously reported by Read et al. (2008). In contrast, the O_3 levels over land typically peak in the afternoon due to the higher concentrations of O_3 precursors (David and Nair, 2011). When bromine and iodine chemistry are excluded, O_3 is reduced primarily by the photolysis of O_3 and its reaction with hydroperoxy radical (HO_2). Adding bromine and iodine chemistry creates more pathways to O_3 reduction. Thus, the bromine and iodine chemistry reduces O_3; however, it does not alter the diurnal profile of O_3. While the diurnal cycle of O_3 without the bromine and iodine chemistry varies slightly with locations due to precursors, meteorology and other factors, the bromine and iodine chemistry does not alter the diurnal cycle at any location but rather simply reduces O_3 concentrations.

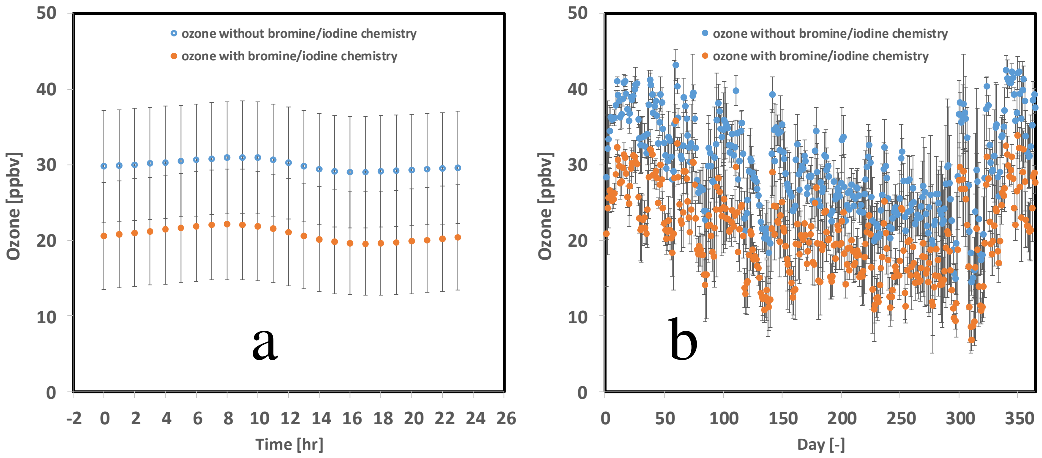

Figure 4. (a) Influence of the bromine and iodine chemistry on diurnal variation of surface O_3 (b) influence of the bromine and iodine chemistry on the day-to-day variation of surface O_3. Blue circle – No_Br/I and red circle – Added_Br/I.

3.4 Influence on the day-to-day variation of O_3

To examine the day-to-day variation of the bromine and iodine chemistry impacts on O_3, we first calculated daily-mean O_3 values for each grid cell over seawater. We then calculated a mean daily value from the same area over the Atlantic Ocean (see Figure 3a). Bromine and iodine chemistry reduces O_3 on each day of the year (Figure 4b), but the magnitude of the reduction varies from day to day. Such variation depends on multiple factors including existing atmospheric O_3 levels and wind speed. The O_3 levels can influence the daily variation in two ways: 1) higher O_3 concentrations increase inorganic iodine emissions which react with and reduce O_3 and 2) higher O_3 increases the reaction rates with bromine and iodine which reduces O_3. Wind speed can influence the daily variation in two ways: 1) lower wind speed enhances inorganic iodine emissions (McDonald et al., 2014) which further reduce O_3 and 2) lower wind speed increases available reaction time between O_3 and bromine/iodine species which can also reduce additional O_3. Bromine and iodine chemistry most efficiently reduces O_3 at low wind speeds and high existing O_3 concentrations.

3.5 Seasonal variation of the influence on O_3

To examine the seasonal variation of the bromine and iodine chemistry impacts on O_3, we first calculated monthly mean O_3 from daily-mean values for each grid cell over seawater. We then calculated a mean value from the same area over the Atlantic Ocean (see Figure 3a). Mean O_3 levels are highest in cooler months and lowest in warmer months (Figure 5) due to the low O_3 precursor levels over seawater that limit O_3 production and cause loss processes to control O_3 concentrations. Photolysis of O_3 and its reaction with HO_2 are two dominant loss processes over seawater (Breton et al., 2017). The loss via photolysis is highest in warmer months due to high actinic flux. Atmospheric HO_2 levels are high in warmer months due to higher photochemical activity; thus, the loss of O_3 via its reaction with HO_2 is also high in warmer months. Bromine and iodine chemistry reduces monthly mean O_3 by ~8-10 ppbv. The reduction of O_3 from bromine and iodine chemistry is largest in December and lowest in July. Bromine and iodine chemistry reduces seasonal mean surface O_3 in Winter (December-February) by 9.9 ppbv, Spring (March-May) by 9.5 ppbv, Summer (June-August) by 8.7 ppbv, and Fall (September-November) by 8.8 ppbv. If the entire seawater is considered, bromine and iodine chemistry reduces mean surface O_3 over seawater by 6.9 ppbv, 6.8 ppbv, 5.9 ppbv, and 6.2 ppbv in Winter, Spring, Summer, and Fall, respectively. Slightly greater O_3 losses occur in the Winter and Spring seasons due primarily to the bromine chemistry and the fact that lower temperatures in cooler months promote efficient partitioning of hydrobromic acid into Br^- which enhances heterogeneous production of ozone-reacting bromine species.

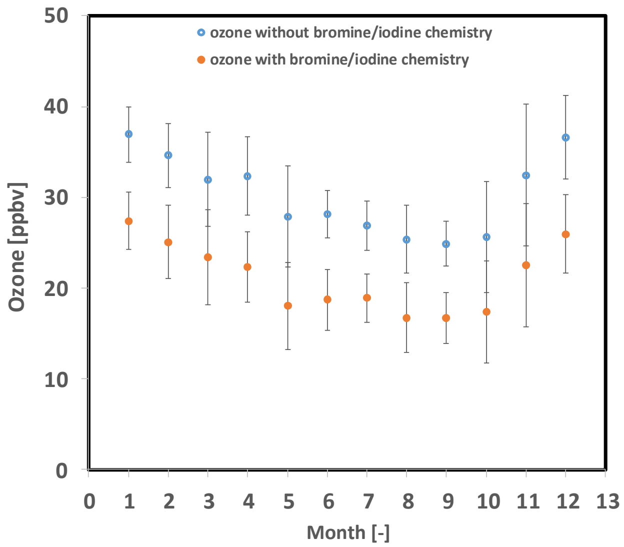

Figure 5. Influence of the bromine and iodine chemistry on month-to-month variation of surface O_3. Error bars are represented with two standard deviation. Blue circle – No_Br/I and orange circle – Added_Br/I

3.6 Influence on background O_3

By comparing the pair of simulations with anthropogenic emission sources over North America zeroed out, we are able estimate the impact of iodine and bromine chemistry on background O_3 over North America. The bromine and iodine chemistry reduces seasonal mean background O_3 over the U.S. in all seasons (Figure 6) with the greatest reduction occuring in the Winter and Spring (2-6 ppbv) followed by the Fall (2-4 ppbv) and Summer (1-3 ppbv). For all seasons, bromine and iodine chemistry reduces more O_3 over the western U.S. and coastal areas than over other inland areas, which is consistent with the results shown in Figure 3b. The springtime reductions in the western U.S. are in areas that have some of the highest background O_3

concentrations in the U.S. (Dolwick, et al., 2016). These substantial reductions in background O_3 from the bromine and iodine chemistry suggest that atmospheric models without this chemistry potentially overpredict background O_3. Our results corroborate the findings of Wang et al. (2015) who reported that halogen chemistry affects the intercontinental transport of O_3.

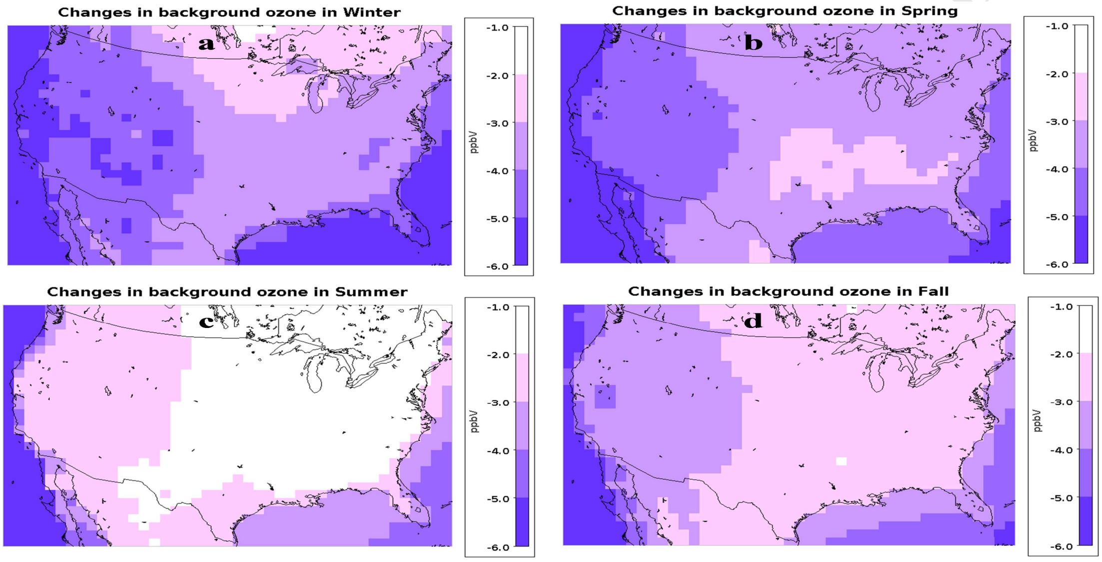

Figure 6. Influence of the bromine and iodine chemistry (Added_Br/I_NoAnth – No_Br/I_NoAnth) on seasonal mean background O_3 over the U.S. (a) Winter (b) Spring (c) Summer (d) Fall. Winter: December- February; Spring: March-May; Summer: June-August; Fall: September-November.

3.7 Isolating the impacts of bromine and iodine chemistry on O_3

Figure 7 shows that bromine and iodine chemistry have different impacts on O_3 concentrations; bromine chemistry reduces annual mean surface O_3 over limited areas of seawater by 2-4 ppbv (Figure 7a) while the iodine chemistry reduces O_3 by 2-10 ppbv over most oceanic areas (Figure 7b). Iodine chemistry affects model prediction over the entire U.S. and reduces annual mean O_3 by 1-2 ppbv over the eastern U.S., 2-3 ppbv over the western U.S., and 3-4 ppbv over some coastal areas. In contrast, bromine chemistry reduces annual mean O_3 by <1 ppbv over U.S. On average, bromine chemistry reduces annual mean O_3 over seawater by 1.2 ppbv while iodine chemistry reduces O_3 by 5.2 ppbv. Iodine chemistry is more efficient in reducing O_3 than the bromine chemistry due to several factors. The rate constant for the I + O_3 reaction is ~10% greater than that of the Br + O_3 reaction (Ordóñez, et al., 2012). Iodine recycles at a faster rate than bromine due to higher photolysis rates of I_2/HOI compared to Br_2/HOBr as well as the presence of higher iodine oxides in the model. Additionally, the inorganic iodine emissions rates are a function of dissolved O_3 and iodide present in seawater (Carpenter et al., 2013) and are higher when atmospheric O_3 concentrations are higher. Such factors in iodine chemistry reduce O_3 over seawater more efficiently than that of bromine chemistry. Lower O_3 concentrations over the marine environment due to iodine chemistry are transported inland resulting in lower O_3 over land.

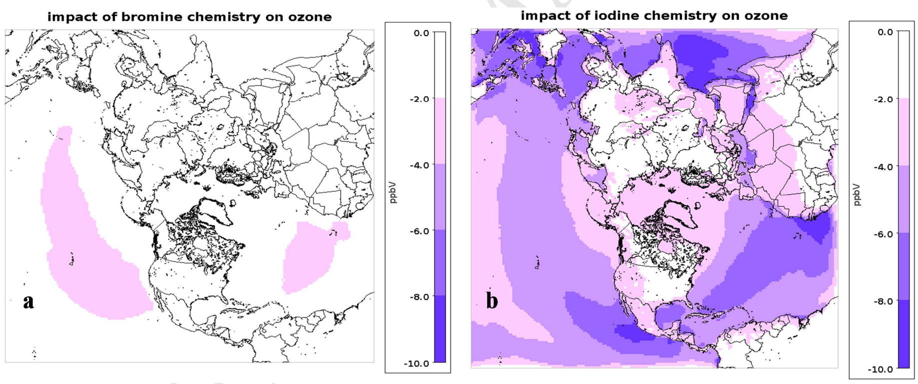

Figure 7. Changes in annual mean surface O_3 with (a) bromine chemistry (Added_Br – No_Br/I) and (b) iodine chemistry (Added_I – No_Br/I)

3.8 Influence of iodine and bromine chemistry on O_3 model performance

In addition to the direct comparison between model simulations, we have also evaluated the simulations without and with bromine and iodine chemistry against both ship-based and land-based O_3 observations. The ship-based surface measurements used for this evaluation are over the Gulf of Mexico from the 2006 Texas Air Quality Study (Parrish et al., 2009b) (TexAQS).

Observed O_3 concentrations during the August 2006 period of the TexAQS campaign are generally less than 30 ppbv, though higher values were measured over some coastal waters off Texas, South Carolina and Georgia (Figure 8a). Model mean bias values (Figure 8b-c) show that neither model simulation captures the high observed values near some coastal waters which results in a negative bias. The model without the bromine and iodine chemistry, however, has a positive bias (median bias +4.7 ppbv) over most areas in the remote ocean while the model with the bromine and iodine chemistry typically has a slight negative bias (median bias -1.0 ppbv, 95% of the observations have a bias within ±30 ppbv) for these areas. We also compared the performance of the simulations without and with bromine and iodine chemistry by calculating the difference in the absolute mean bias between the two simulations. In this calculation, positive values mean that the simulation with bromine and iodine chemistry has a higher absolute bias (further from observations) while negative values indicate that it has a lower absolute bias (closer to observations). The difference in absolute mean bias shown in Figure 8d reveals that the inclusion of bromine and iodine chemistry generally reduces the bias by 2-6 ppbv over the ocean without much degradation in other regions.

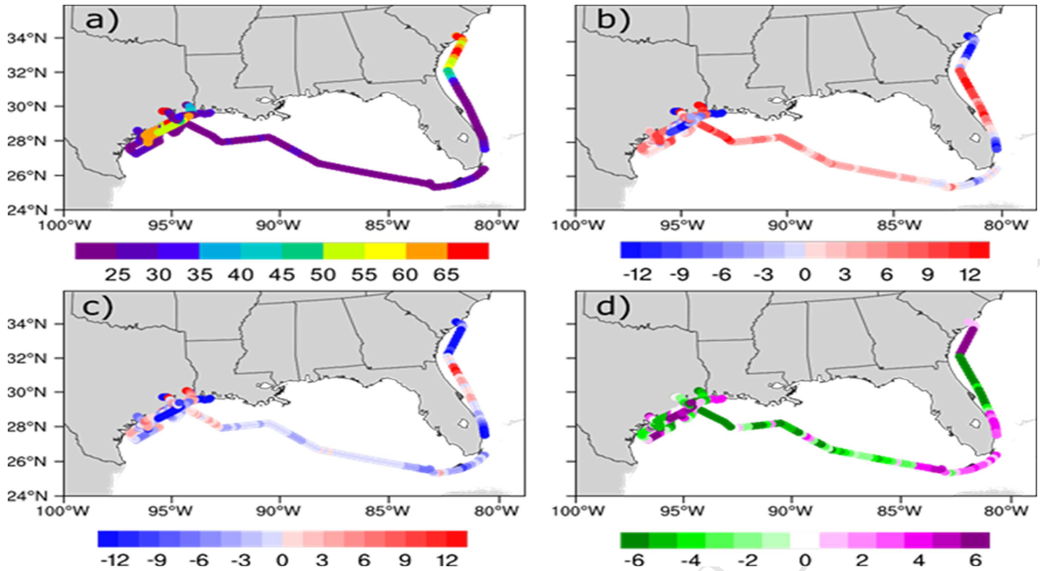

Figure 8. (a) Observed surface O_3 concentrations from R/V Ronald H. Brown during August 2006 of the TexAQS campaign (Parrish et al., 2009b) (b) model mean bias for the model without any bromine and iodine chemistry (No_Br/I – Observations) (c) model mean bias for the model with the bromine and iodine chemistry (Added_Br/I – Observations), and (d) differences in the model absolute mean bias between simulations without and with bromine and iodine chemistry (|Added_Br/I – Observations| – |No_Br/I – Observations|). The green colors in (d) represent locations where the simulation with the bromine and iodine chemistry had a lower model bias (improved prediction), and purple colors represent locations where the simulation with the bromine and iodine chemistry had a higher model bias (worse prediction). All units are in ppbv.

The simulations without and with bromine and iodine chemistry were also evaluated against observations in the U.S. from the Clean Air Status and Trends Network (CASTNET) and the USEPA's Air Quality System (AQS). CASTNET and AQS include sites at mainly remote and mainly urban locations, respectively. Monthly mean bias for the simulation without the bromine and iodine chemistry varies (-8 to +4 ppbv for CASTNET sites and -3 to +7 ppbv for AQS sites), with negative biases (underprediction) for several months (January - August and December at CASTNET sites and April – June for AQS sites) and positive biases (overprediction) for other months (Figure 9). The inclusion of bromine and iodine chemistry generally improves O_3 predictions in the Fall at both the CASTNET and AQS sites and deteriorates the model predictions in the Spring. In the Winter and Summer, the simulation with bromine and iodine chemistry generally has degraded predictions at the CASTNET sites and improved predictions at the AQS sites.

When only the coastal sites are considered, the monthly mean biases for the simulation without bromine and iodine chemistry are positive for January – February and July - December at CASTNET sites (Figure 10a) and for all months at AQS sites (Figure 10b). Differences between the simulations without and with bromine and iodine chemistry are more noticeable for the coastal sites, with a larger number of months having improved predictions when bromine and iodine chemistry is included. This is especially true at coastal AQS sites where the bromine and iodine chemistry improves model performance for all months except March and April. Gantt et al. (2017) compared model (using a 12-km horizontal grid resolution) predictions for August 2006 with observations from the 2006 ship-based TexAQS and coastal AQS sites and reported that the model without bromine and iodine chemistry generally over-predicts O_3 while the bromine and iodine chemistry improves the model performance. Model performance shown in Figures 8 and 10 for August is consistent with results of Gantt et al. (2017).

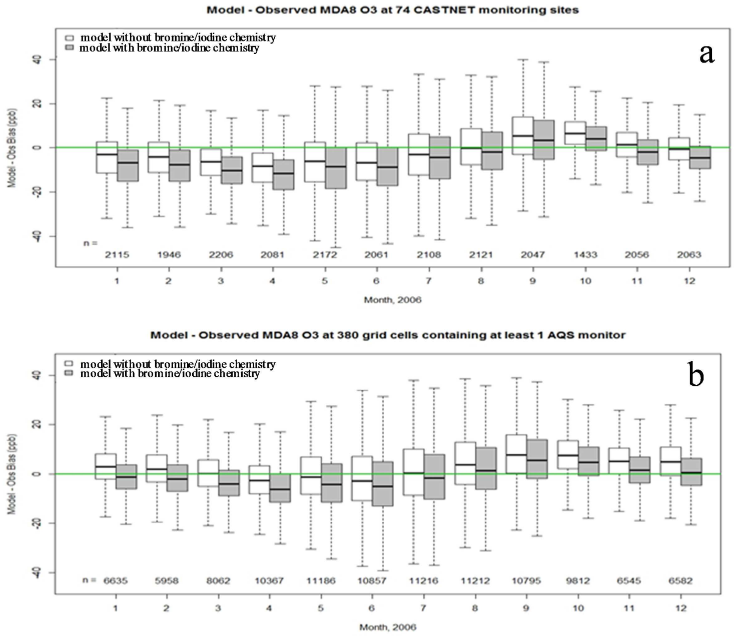

Figure 9. Monthly mean bias without (No_Br/I – Observations) and with (Added_Br/I – Observations) the bromine and iodine chemistry at all (a) CASTNET and (b) AQS sites. AQS observations falling within the same grid cell are first averaged prior to comparing to the model value. Lower bar in the box represents the 25th percentile, middle bar represents the median and the upper bar represents the 75 percentile values. The lowest horizontal bar represents the minimum value while the highest horizontal bar represents the maximum value.

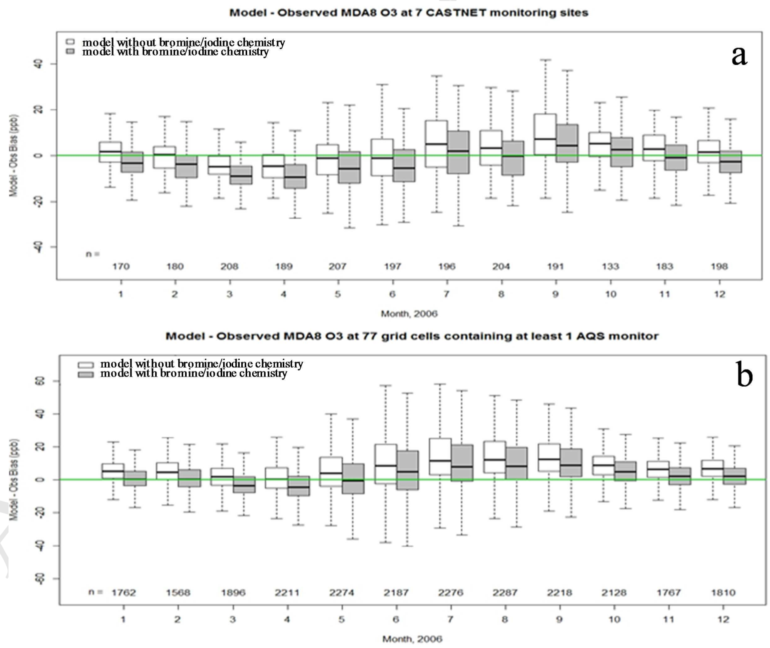

Figure 10. Monthly mean bias without (No_Br/I – Observations) and with (Added_Br/I – Observations) the bromine and iodine chemistry at coastal (a) CASTNET and (b) AQS sites. AQS observations falling within the same grid cell are first averaged prior to comparing to the model value. Lower bar in the box represents the 25th percentile, middle

bar represents the median and the upper bar represents the 75 percentile values. The lowest horizontal bar represents the minimum value while the highest horizontal bar represents the maximum value.

The hemispheric domain also allows for model evaluation against O_3 observations from monitors in Japan as part of the Acid Deposition Monitoring Network in East Asia (www.eanet.asia/eanet) (Figure 11). The simulation without bromine and iodine chemistry underpredicts O_3 (by 2-9 ppbv) during the cooler months (January-May and November) and overpredicts (by 2-19 ppbv) in the warmer months (June-September). Including bromine and iodine chemistry further deteriorates O_3 model performance in the cooler months but improves model performance in warmer months. This seasonality is consistent with Kyo et al. (2019) which reported CMAQ overpredictions of O_3 during the summertime over Japan.

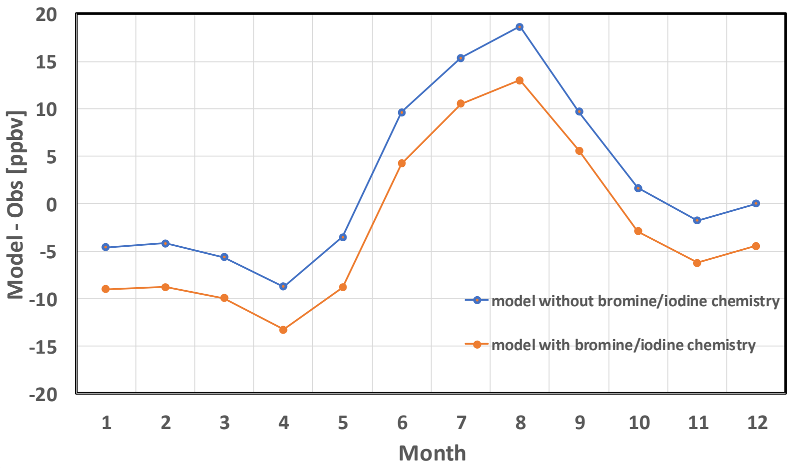

Figure 11. Monthly mean bias without (No_Br/I – Observations) and with (Added_Br/I – Observations) the bromine and iodine chemistry at monitoring sites in Japan.

4.0 SUMMARY

Regional chemical transport models like CMAQ are routinely applied to specific geographic areas for developing air pollutant control strategies. Often the boundary conditions for the regional models are adapted from hemispheric and global models to capture the broader influence of global pollution on the focal region. The results of this study reveal that bromine and iodine chemistry not only affects O_3 over seawater but also over land, improves model performance for coastal sites, and reduces the predicted background ozone. These combined impacts provide strong evidence that bromine and iodine chemistry should be considered for inclusion in air quality models used for O_3 applications.

DISCLAIMER

The views expressed in this paper are those of the authors and do not necessarily represent the views or policies of the U.S. EPA.

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Highlights

- Bromine and iodine chemistry reduces ozone
- Iodine chemistry is more effective in reducing ozone than the bromine chemistry
- Bromine and iodine chemistry affects background ozone
- Bromine and iodine chemistry improves model performance

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: