

RESEARCH LETTER

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Key Points:

- Injection of iodine to the stratosphere can be 2 to 5 times larger than accepted upper limits
- Iodine catalytic cycles could account for up to 30% of ozone loss in the tropical lower stratosphere
- Iodine-mediated depletion of stratospheric ozone can be comparable to that of VSL bromocarbons

Supporting Information:

- Supporting Information S1

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Injection of iodine to the stratosphere

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Abstract We report a new estimation of the injection of iodine into the stratosphere based on novel daytime (solar zenith angle < 45°) aircraft observations in the tropical tropopause layer and a global atmospheric model with the most recent knowledge about iodine photochemistry. The results indicate that significant levels of total reactive iodine (0.25–0.7 parts per trillion by volume), between 2 and 5 times larger than the accepted upper limits, can be injected into the stratosphere via tropical convective outflow. At these iodine levels, modeled iodine catalytic cycles account for up to 30% of the contemporary ozone loss in the tropical lower stratosphere and can exert a stratospheric ozone depletion potential equivalent to, or even larger than, that of very short-lived bromocarbons. Therefore, we suggest that iodine sources and chemistry need to be considered in assessments of the historical and future evolution of the stratospheric ozone layer.

1. Introduction

Most of the chlorine and bromine that reaches the stratosphere, where they catalytically destroy ozone, originates from anthropogenic emissions of long-lived halogenated compounds [Solomon, 1999], which have been addressed under the Montreal Protocol. However, a portion of ozone depletion in the stratosphere can be attributed to natural oceanic emissions and transport to the stratosphere of very short-lived brominated substances (VSL^{Br}) [Salawitch, 2006]. The most recent estimates indicate that between 2 and 8 parts per trillion by volume (pptv) of VSL^{Br} are injected to the stratosphere [World Meteorological Organization (WMO), 2014]. In the case of iodine, the oceans provide the main source of iodine compounds to the atmosphere [Carpenter et al., 2013; Saiz-Lopez et al., 2012a] where they reduce the global warming effect of ozone in the marine troposphere [Saiz-Lopez et al., 2012b]. Recent studies have reported values of 0.2–0.4 pptv of iodine monoxide (IO) in the free troposphere over the subtropical station of Izaña in the Atlantic Ocean (Canary Islands) [Puertedura et al., 2012] and 0.1–0.2 pptv range throughout the tropical free troposphere of the Pacific Ocean [Dix et al., 2013], demonstrating the ubiquitous presence of the radical in the marine free troposphere. However, due to the low levels of iodine monoxide (IO) previously detected in the lowermost stratosphere at twilight (solar zenith angle (SZA) ~90°) [Butz et al., 2009; Wennberg et al., 1997], iodine chemistry is not considered in the photochemistry of stratospheric ozone [WMO, 2014].

There have been several attempts to detect iodine oxides (IO and OIO) in the upper troposphere-lower stratosphere [Berthet et al., 2003; Bösch et al., 2003; Butz et al., 2009; Pundt et al., 1998; Wennberg et al., 1997; Wittrock et al., 2000]. Ground-based observations in Arizona (United States) determined an upper limit for total inorganic iodine (I_y) of 0.2 pptv in the stratosphere [Wennberg et al., 1997]. Balloon-borne UV-Visible spectra derived lower stratospheric upper limits of around 0.1 pptv for both IO and OIO in the northern high and middle latitudes [Bösch et al., 2003], as well as over the tropics [Butz et al., 2009], consistent with previous reports. There is, however, one exception of a study reporting stratospheric IO mixing ratios of 0.65 and 0.8 pptv above Spitzbergen [Wittrock et al., 2000].

The first report on the potential impact of iodine on stratospheric ozone showed that a hypothetical stratospheric iodine loading of 1 pptv could be of substantial importance to ozone loss in the lowermost stratosphere [Solomon et al., 1994]. Since then, the subsequent World Meteorological Organization (WMO) and United Nations Environment Programme Ozone Assessment Reports [WMO, 2014], based on available remote-sensing measurements at twilight [Berthet et al., 2003; Bösch et al., 2003; Butz et al., 2009; Pundt et al., 1998;

Wennberg *et al.*, 1997], suggested upper limits of 0.1 pptv of IO and a total I_y of <0.15 pptv, leading to an estimated negligible role of iodinated gases on stratospheric ozone photochemistry [WMO, 2014]. Consequently, global assessments on climate change have thus far only considered the stratospheric ozone depletion potential of long- and short-lived bromocarbons and chlorocarbons [WMO, 2014].

In this study, we combine aircraft measurements of IO vertical profiles in the tropical tropopause layer (TTL) with a chemistry-climate model that includes state-of-the-art iodine photochemistry to provide a new estimate of the stratospheric injection of iodine.

2. Aircraft Observations

IO vertical profiles were measured over the tropical Eastern Pacific Ocean (tEPO) by the University of Colorado Airborne Multi AXis Differential Optical Absorption Spectroscopy (CU AMAX-DOAS) instrument aboard the National Science Foundation/National Center for Atmospheric Research Gulfstream V aircraft (NSF/NCAR GV). Measurements were made in the Northern Hemisphere (NH) and Southern Hemisphere (SH) tropics during the Tropical Ocean Troposphere Exchange of Reactive halogen species and Oxygenated VOC (TORERO) project (January/February 2012) [Volkamer *et al.*, 2015], in an area categorized as preindustrial environment [Carslaw *et al.*, 2013]. All research flights (RF01, RF12, RF14, and RF17) targeted remote pristine marine conditions, cloud free, and aged air in the tropical free troposphere. The flight tracks, dates, profile times, and coordinates of the locations for profile case studies are shown in the supporting information. These flights probed pristine marine air below 2 km and did not show signs of land influences inside the marine boundary layer (MBL), as indicated by CO concentrations that were generally well below 100 ppbv; the lowest MBL-CO was 50 ppbv (RF01), and the highest MBL-CO was 109 ppbv (RF17). Some minor pollution influences were observed between 2 and 8 km (~ 25 pptv NO_2 during RF12 and RF17, both NH) [Volkamer *et al.*, 2015], but no evidence for pollution was observed in the SH. Above 12 km, CO was between 50 and 60 ppbv for all research flights. Analysis of 7 day back trajectories and tracer measurements on board further showed consistently that the air above 10 km had spent more than 85% of the time in the upper FT (RF01, RF12, and RF14). These trajectories further showed influences from tropical deep convection, which were generally more prominent in the lower and middle FT, and had happened 3–7 days prior to flights RF01, RF12, and RF14. During RF17 deep convection influences were more recent, and stronger below 5–6 km, and weaker but nonzero over the full altitude range probed. Further details about the TORERO project are described in a previous work [Volkamer *et al.*, 2015].

The CU AMAX-DOAS instrument, its data analysis, and profile retrieval have been described in detail elsewhere [Baidar *et al.*, 2013; Dix *et al.*, 2013; Volkamer *et al.*, 2015]. Briefly, the instrument collects spectra of scattered sunlight from well-defined lines of sight above, below, and forward of the aircraft. The limb scanning telescope has a vertical dispersion of 0.17° and is actively angle stabilized to better 0.2° accuracy in real time [Baidar *et al.*, 2013]. Spectra were analyzed using the DOAS method [Platt and Stutz, 2008] and the WinDOAS software package. The DOAS analysis procedure used to evaluate IO and $\text{O}_2\text{-O}_2$ oxygen collision complexes (O_4) has previously been described [Volkamer *et al.*, 2015]. A fixed reference spectrum is used to account for Fraunhofer lines in the solar atmosphere and chosen to minimize contamination with the trace gas of interest and maximize signal to noise. Details on selected references are included in Table S1 in the supporting information. IO concentration profiles were retrieved by optimal estimation inversion of measured differential slant column density (dSCD), using spectra with elevation angle 0° only, i.e., horizontal and forward of the plane, and their respective weighting functions computed using the fully spherical Monte Carlo radiative transfer model McArtim [Deutschmann *et al.*, 2011]. Radiation fields were constrained by in situ pressure, temperature, and water vapor measurements as well as by CU AMAX-DOAS observations of O_4 at 477 nm [Volkamer *et al.*, 2015].

3. Model and Experiments

The global 3-D chemistry-climate model CAM-Chem (Community Atmospheric Model with chemistry, version 4.0) includes a comprehensive benchmark chemistry scheme to simulate the evolution of trace gases and aerosols in the troposphere and the stratosphere [Lamarque *et al.*, 2012]. The model has been merged with a state-of-the-art halogen chemistry scheme for both iodine and bromine species, covering both the troposphere and lower to middle stratosphere [Fernandez *et al.*, 2014; Saiz-Lopez *et al.*, 2014]. This includes

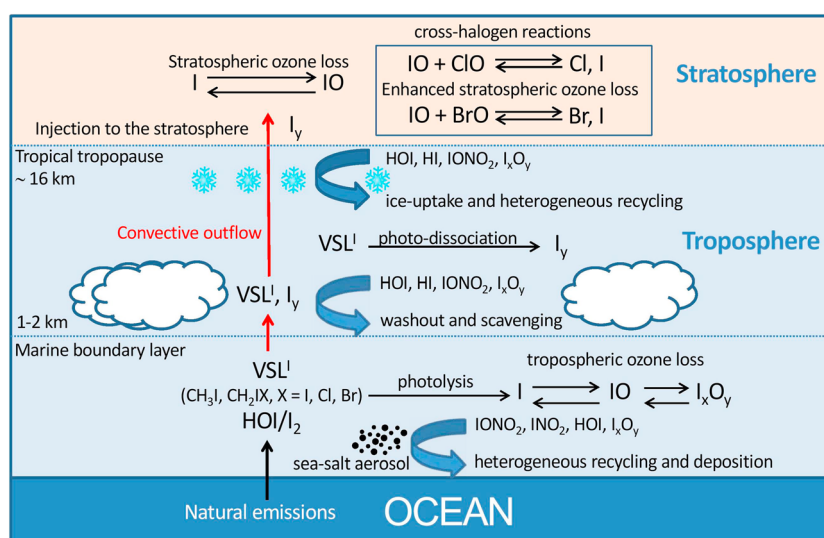


Figure 1. Atmospheric chemistry of iodine. The oceans release a suite of very short-lived iodocarbons VSL^{I} and inorganic ($\text{HOI} + \text{I}_2$) species that are rapidly photolyzed and react with atmospheric ozone, nitrogen, and hydrogen oxides. The resulting reactive (e.g., I and IO) and reservoir (e.g., IONO_2 and HOI) species, along with CH_3I compounds, are transported by convection to the upper troposphere, where the competition of recycling and removal process on liquid-ice clouds define the total iodine burden; while the rapid gaseous chemical cycling defines the relative partitioning between species. Further injection of reactive iodine to the stratosphere potentially influences stratospheric ozone levels through efficient catalytic ozone destruction cycles (including interhalogen cross reactions) comparable to those caused by bromine and chlorine.

the photochemical breakdown of five very short-lived bromocarbons ($\text{VSL}^{\text{Br}} = \text{CHBr}_3, \text{CH}_2\text{Br}_2, \text{CH}_2\text{BrCl}, \text{CHBrCl}_2$, and CHBr_2Cl) and four iodocarbons ($\text{VSL}^{\text{I}} = \text{CH}_3\text{I}, \text{CH}_2\text{I}, \text{CH}_2\text{IBr}$, and CH_2I_2) which are naturally emitted from the ocean to the atmosphere [Ordóñez *et al.*, 2012]. The lifetimes of CH_2I , CH_2IBr , and CH_2I_2 range from hour to minutes, while for CH_3I it is in the order of 1 week. As a consequence, CH_3I is the main iodocarbon in the model that, through efficient transport within deep convection cells, is expected to reach the TTL. Additionally, abiotic oceanic sources of HOI and I_2 have been included in the lowest layer of the model, based on recent laboratory studies of the oxidation of aqueous iodide by atmospheric ozone deposited on the ocean surface [Carpenter *et al.*, 2013]. Figure 1 summarizes in a simplified schematic the main gas- and condensed-phase iodine photochemistry processes in the troposphere and stratosphere.

In this work, CAM-Chem was configured with a horizontal resolution of 1.9° latitude by 2.5° longitude and 26 levels, from the surface to ~ 40 km (with eight levels above 100 hPa) as done in previous studies [Fernandez *et al.*, 2014; Saiz-Lopez *et al.*, 2014]. The model runs have been performed in specified dynamics mode [Lamarque *et al.*, 2012]. A period of 15 years was required to ensure stratospheric stabilization of all halogen species. Besides the standard 24 h averaged streaming, time-dependent output for day and night has been generated considering the noon (11:30–12:30) and midnight (23:30–00:30) local times, respectively, for all latitudes and longitudes. Tropical annual averages have been computed between 20°N and 20°S .

The chemical mechanism is an update based on the scheme of higher order iodine oxides photolysis explicitly defined in previous work [Saiz-Lopez *et al.*, 2014], with the inclusion of heterogeneous recycling reactions occurring on the surface of ice particles in the upper troposphere. The ice-mediated reactions for halogen species are key processes in the TTL because they control the halogen burden prior to stratospheric injection through the competition between effective ice-uptake (removal) and reactive ice-uptake (recycling) [Fernandez *et al.*, 2014]. As ice-mediated heterogeneous reactions have been suggested to occur to bromine species in the TTL [Aschmann and Sinnhuber, 2013], we have assumed equivalent processes for iodine reservoirs. However, the heterogeneous recycling of iodine species on ice particles remains unexplored [Saiz-Lopez *et al.*, 2012a], and therefore, two different sets of simulations have been performed to account for the impact of heterogeneous uptake: the ice-recycling and non-recycling schemes of the main iodine reservoir species, hypoiodous acid (HOI), and iodine nitrate (IONO_2). The recycling reactions rates were computed by means of the free regime approximation [McFiggans *et al.*, 2000], which considers that the

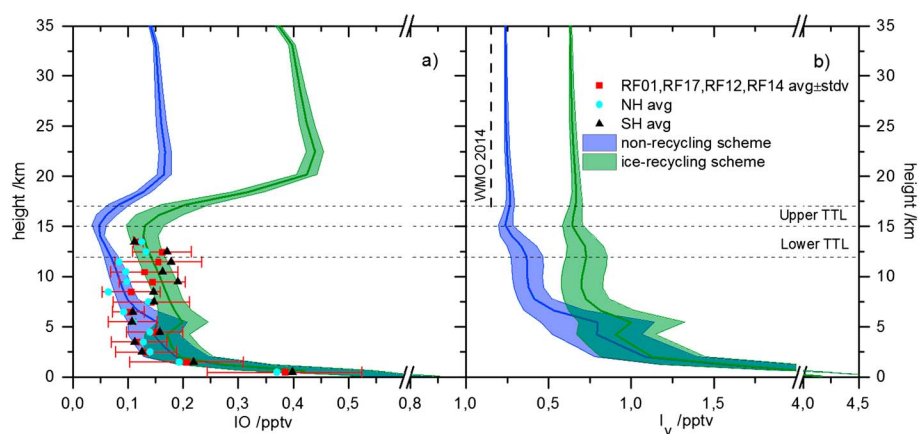


Figure 2. Vertical distribution of (a) IO measured in the tropical troposphere and modeled daytime IO and (b) modeled I_y concentrations for both ice-recycling (green) and non-recycling (blue) schemes. Red squares represent the average and standard deviation ($\pm\sigma$) of the four flights, while cyan circles and black triangles account for the average of Northern (RF12 and RF17) and Southern (RF01 and RF14) Hemisphere flights, respectively. Shaded area represents the annual average with the standard deviation of modeled values ($\pm\sigma$) within the tropics (20°S – 20°N). I_y is defined as the sum of $I + IO + HOI + IONO_2 + (2 \times I_xO_y) + I_{\text{minor}} + (2 \times I_2) + IBr + ICl$, where I_xO_y includes $I_2O_2 + I_2O_3 + I_2O_4$, and I_{minor} is defined as $HI + OIO + INO_2 + INO$. TTL is defined as the layer with a bottom boundary at the region of maximum convective outflow (~ 12 km) and an upper limit coincident with the tropical cold point tropopause at about 17 km.

rate-limiting step is the uptake of halogen species on the ice crystal surface. Additionally, scavenging process for inorganic iodine species was computed following the Neu and Prather approach [Neu and Prather, 2012].

Both mechanisms include heterogeneous recycling of HOI, $IONO_2$, and INO_2 on sea-salt aerosols within the lower troposphere [Saiz-Lopez et al., 2014], and the additional removal of HOI, HI, $IONO_2$, and I_xO_y either by nonreactive washout [Neu and Prather, 2012] in liquid clouds or by effective ice-uptake within the TTL. A summary including the details of the two independent simulations and the ice recycling heterogeneous reactions included for chlorine, bromine, and iodine, together with their reactive coefficients (γ) are shown in the supporting information.

Additional independent simulations were performed maintaining identical iodine chemistry and sources, but including and neglecting the contribution from VSL bromocarbons. In this way, the total inorganic bromine (Br_y) burden due to long-lived sources (Br_y^{LL}) and from very short-lived sources (Br_y^{VSL}) can be separated. The purpose of these simulations is to isolate the ozone-depleting potential of each group of halocarbons (LL versus VSL) at different heights. In this way, the contribution to ozone depletion arising from the natural VSL^{Br} sources can be directly compared to the additional contribution from iodine-mediated catalytic cycles due to VSL^{I} .

4. Results and Discussion

4.1. Measurements and Model Comparisons

Figure 2 shows the average IO profile from four research flights recorded in the NH (RF12 and RF17) and SH (RF01 and RF14) (see flight tracks and individual profiles in the supporting information). Under overhead Sun conditions ($5^\circ < \text{SZA} < 45^\circ$) we have detected $\sim 0.14 \pm 0.04$ pptv IO in the lower TTL (12–14 km altitude). We find that IO in the SH-lower TTL closely resembles that in the NH-lower TTL (NH: 0.13 ± 0.04 pptv; SH: 0.15 ± 0.04 pptv; 12–14 km). Given this rather constant IO mixing ratio in the lower TTL of both hemispheres we have combined the new IO profiles and use the average tropical IO profile to reevaluate previous estimates of stratospheric iodine injection.

While most of the gas-phase iodine chemistry is relatively well documented (Figure 1) [Saiz-Lopez et al., 2012a], a key uncertainty in the tropical upper troposphere is ice-mediated heterogeneous reactions, since these are key processes that determine the inorganic halogen burden prior to stratospheric injection [Aschmann and Sinnhuber, 2013; Fernandez et al., 2014]. Consequently, we use the model to perform sensitivity studies

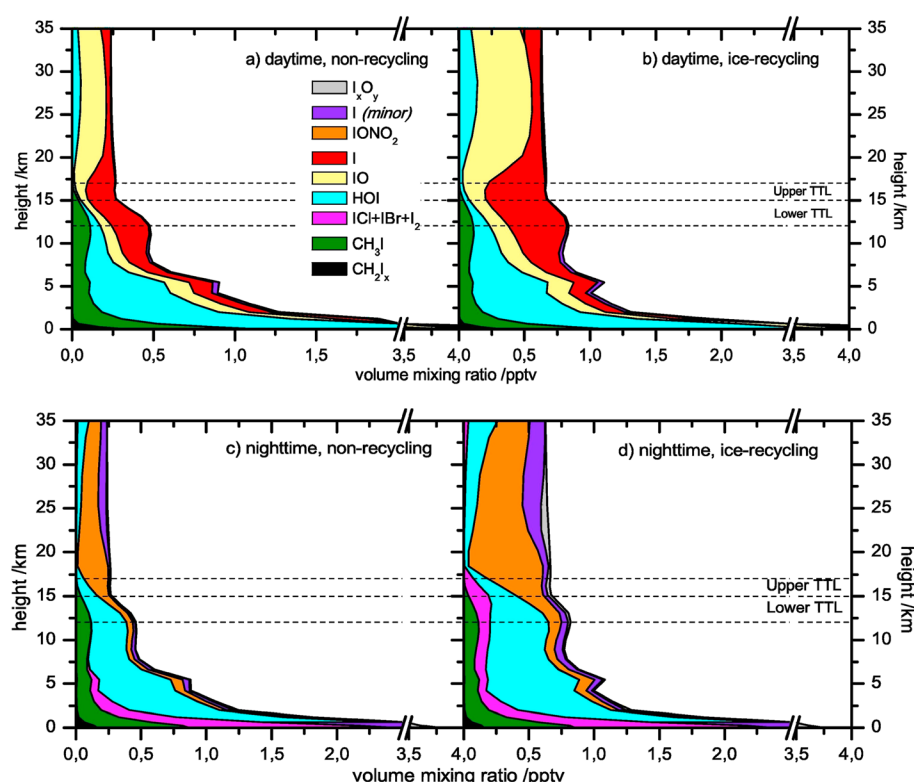


Figure 3. Predicted vertical partitioning of iodine species averaged over the tropics at (a and b) daytime and (c and d) nighttime, for ice recycling (Figures 3b and 3d) and nonrecycling (Figures 3a and 3c) schemes.

and simulate iodine levels with (ice-recycling) and without (non-recycling) heterogeneous recycling on airborne ice crystals.

The aircraft observations show that IO occurs throughout the tropical free troposphere with averaged mixing ratios ranging 0.1–0.2 pptv (Figure 2a). Previous measurements of FT-IO are limited to the NH and are generally consistent with the IO we find over the SH tEPO at altitudes where there is overlap. Around 2 km altitude, 0.2–0.4 pptv have been measured over the NH Atlantic Ocean [Puentedura *et al.*, 2012], 0.1 pptv IO up to 10 km over the NH tCPO (Central Pacific Ocean) [Dix *et al.*, 2013], and 0.1–0.2 pptv IO up to 14 km over the NH tEPO [Volkamer *et al.*, 2015]. Notably, IO in the lower TTL is slightly higher than previous measurements at lower altitudes in the NH and consistent between both hemispheres, indicating that IO in the lower TTL is widespread. Note also that other recent observations of IO profiles in the tropics found no indication for lower IO in flights under stratospheric influences [Wang *et al.*, 2015]. The modeled IO profiles are in reasonable agreement with the measurements in the lower troposphere. These simulations provide rather consistent ranges of iodine concentrations that account for the tropical annual variability in the model and the uncertainty in the nature of gas-ice phase interactions of iodine species in the upper troposphere. The IO profiles differ significantly in the middle and upper troposphere, where the average IO between 12 and 14 km altitude for the flight locations corresponds to $\sim 0.06 \pm 0.01$ pptv, and $\sim 0.14 \pm 0.02$ pptv in the non-recycling and ice-recycling simulations. Only the model that represents iodine recycling on ice particles can explain the measured IO in the lower TTL (Figure 2a).

4.2. Stratospheric Injection of Iodine

We next calculate the resulting levels of I_y injected to the stratosphere for both independent simulations (Figure 2b). Using the non-recycling scheme the model estimates an I_y value of ~ 0.25 pptv at the tropical tropopause (~ 17 km), which is 67% higher than the upper limit <0.15 pptv recommended by WMO [2014]. However, the non-recycling scheme underestimates the observations significantly in the lower TTL (Figure 2a). Remarkably, this model measurement mismatch can be fully accounted for by simply considering heterogeneous recycling on ice surfaces in the model. In that case, the calculated total iodine

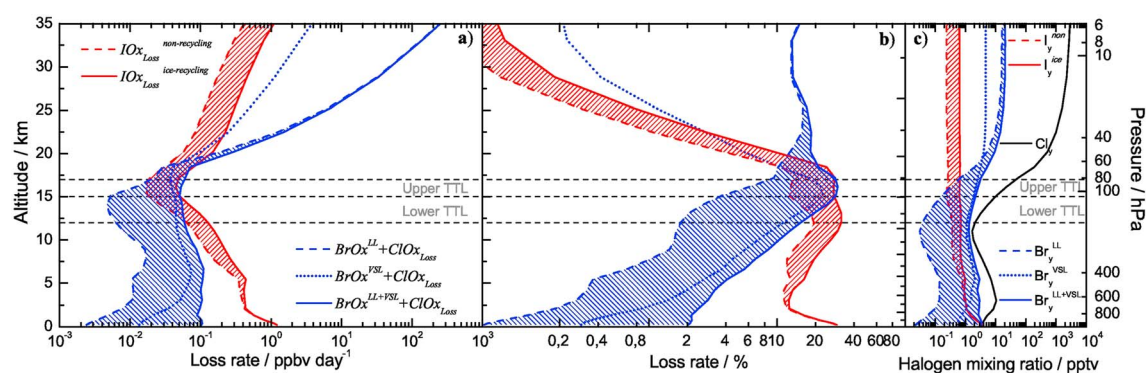


Figure 4. Modeled halogen-mediated ozone loss in the tropical atmosphere for both ice-recycling and non-recycling schemes: (a) absolute loss rate for the grouped BrO_x + ClO_x and IO_x families. The independent contribution of long-lived (LL) and very short-lived (VSL) bromine to the BrO_x + ClO_x family is shown by dashed and dotted lines, respectively; (b) percentage contribution of each family to the total loss rate; and (c) vertical profiles of the Br_y, Cl_y, and I_y families.

injection to the stratosphere reaches ~ 0.7 pptv, which is 4.5 times larger than the current WMO upper limit estimates [WMO, 2014]. Interestingly, either simulation implies that significantly more reactive iodine is injected to the stratosphere than currently thought [WMO, 2014].

It is worth noting that the IO occultation measurements, upon which the current estimates of stratospheric iodine injection are based, are performed at high SZA $\sim 85^\circ$ – 90° and this has some important ramifications. Measurements made at twilight capture the end of the typical top-hat-shaped diurnal profile of IO (supplementary information), when most of the IO is rapidly converted into nighttime reservoir species (IONO₂ and HOI) (Figure 3 and supplementary information). We have performed a model run with assimilated meteorology simulating the location and atmospheric conditions of previous balloon-borne solar occultation measurements [Butz *et al.*, 2009]. Our modeled IO throughout the upper troposphere and lower stratosphere at twilight is in very good accord with the solar occultation method IO upper limits, < 0.1 pptv. However, our model simulation predicts up to four times higher total iodine levels, I_y, in the stratosphere (see supporting information). Since the early estimates of stratospheric iodine injection [Butz *et al.*, 2009; Wennberg *et al.*, 1997; WMO, 2014] our understanding of iodine photochemistry has advanced in recent years, and the importance of IO photolysis, treatment of IONO₂ photodissociation, and mainly the formation and photochemistry of the higher I_xO_y species (e.g., I₂O₂, I₂O₃, and I₂O₄) [Saiz-Lopez *et al.*, 2012a] have been shown to influence the transport and burden of iodine in the middle and upper troposphere [Saiz-Lopez *et al.*, 2014, 2012a]. These advances are represented in the state-of-the-art CAM-Chem model. Consistent with the observed IO amounts at twilight (< 0.1 pptv IO at SZA $\sim 90^\circ$ [Butz *et al.*, 2009] and 0.1 – 0.2 pptv IO for $85^\circ < \text{SZA} < 88^\circ$ [Wennberg *et al.*, 1997]), the model predicts more I_y primarily because we consider the highly photolabile I_xO_y species as part of I_y [Saiz-Lopez *et al.*, 2014, 2012a], which had been ignored in earlier estimates. Their inclusion results in higher levels of I_y, particularly in the form of HOI and IONO₂ at twilight when their photolysis back to reactive species is very slow. Moreover, in the tropics the solar terminator for photochemistry under twilight conditions moves much faster than in the midlatitudes, which accelerates the conversion of reactive species into reservoir species during tropical sunsets. An important difference consists in the treatment of IONO₂ photolysis to form I + NO₃ (rather than IO + NO₂), which limits the persistence of IO through the sunset in the TTL, where the I + O₃ reaction is not very efficient due to the cold prevailing temperatures. At 20 km, CAM-Chem predicts 0.43, 0.11, and 0.02 pptv IO for SZA 80° , 87° , and 94° , respectively, in good agreement with previous observations [Butz *et al.*, 2009; Wennberg *et al.*, 1997]. Because most of the I_y is actually present in reservoir species at twilight, the previous IO measurements at high SZA could likely represent lower limits, instead of the accepted upper limits [WMO, 2014] of the amount of iodine reaching the stratosphere (Figure 2).

4.3. Effect on Ozone

We used the model to compute the contribution of iodine chemistry to tropical lower to middle stratospheric ozone loss (IO_x) (Figure 4). Up to the bottom of the TTL, IO_x is the main halogen contributor to ozone depletion, exceeding the combined effect of total bromine (arising from long- and short-lived sources) and

chlorine, $\text{BrO}_x^{\text{LL}+\text{VSL}} + \text{ClO}_x$ (Figure 4). Remarkably, we calculate that iodine-mediated ozone loss in the tropical lower stratosphere (ranging 15–30% of total ozone loss between 17 and 20 km altitude) is comparable to, or even surpass, the rate of ozone loss caused by the sum of VSL^{Br} and stratospheric chlorine, $\text{BrO}_x^{\text{VSL}} + \text{ClO}_x$, up to about 25 km (Figure 4). The contribution of iodine to lower stratospheric ozone loss, even at low concentrations, results from a twofold effect, (i) regeneration of I atoms involves efficient ozone-depleting catalytic cycles, which are much more efficient than those for bromine and chlorine radicals [Solomon *et al.*, 1994], and (ii) interhalogen cross reactions represent an added factor by which iodine enhances stratospheric ozone depletion as the additional IO provides a new efficient reaction partner for BrO and ClO (Figure 1). At 20 km in the tropics, the ice-recycling scheme yields a total halogen-mediated O_3 destruction of 0.44 parts per billion by volume (ppbv) d^{-1} , with percentage contributions of 43, 23, and 34 % attributed to $(\text{BrO}_x^{\text{VSL}} + \text{ClO}_x)$, $(\text{BrO}_x^{\text{LL}} + \text{ClO}_x)$ and IO_x , respectively (Figure 4). This significant increase in the depletion rate resulting from the coupled iodine, bromine, and chlorine chemistry (0.44 ppbv d^{-1} , 28% of total ozone loss at 20 km in the tropical stratosphere), compared to bromine and chlorine alone (0.29 ppbv d^{-1} , 18% of total ozone loss), is currently ignored in simulations of ozone depletion in the stratosphere [WMO, 2014].

5. Concluding Remarks

The combination of aircraft IO profile observations together with two modeling approaches leads us to the conclusion that injection of iodine to the stratosphere can be larger than currently considered. The unaccounted levels of stratospheric iodine may have large implications in stratospheric photochemistry and overall stratospheric ozone depletion. Even at these sub-ppbv stratospheric iodine levels, iodine atom-catalyzed ozone depletion could likely play a significant role in current stratospheric ozone chemistry. Furthermore, we suggest that this contribution of natural iodine to stratospheric ozone destruction will be more significant in the future evolution of the ozone layer as the concentration of anthropogenic ozone-depleting substances in the stratosphere decreases. Further measurements of the different iodine species, and their associated processes, in the upper troposphere and lower stratosphere are critical to obtain accurate estimates of the abundance of stratospheric iodine.

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