



RESEARCH LETTER

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Key Points:

- Low ozone and cold temperatures increase atomic halogen abundances in the TTL
- Measurements of atomic halogens are required to constrain the halogen budget in global models
- The tropical rings of atomic halogens link ocean biogeochemistry, tropospheric ozone, and temperature

Supporting Information:

- Supporting Information S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Figure S6
- Movie S1

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On the formation of tropical rings of atomic halogens: Causes and implications

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Abstract Halogens produced by ocean biological and photochemical processes reach the tropical tropopause layer (TTL), where cold temperatures and the prevailing low ozone abundances favor the diurnal photochemical enhancement of halogen atoms. Under these conditions atomic bromine and iodine are modeled to be the dominant inorganic halogen species in the sunlit TTL, surpassing the abundance of the commonly targeted IO and BrO radicals. We suggest that due to the rapid photochemical equilibrium between halogen oxides and halogen atoms a natural atmospheric phenomenon evolves, which we have collectively termed “tropical rings of atomic halogens.” We describe the main causes controlling the modeled appearance and variability of these superposed rings of bare bromine and iodine atoms that circle the tropics following the Sun. Some potential implications for atmospheric oxidizing capacity are also explored. Our model results suggest that if experimentally confirmed, the extent and intensity of the halogen rings would directly respond to changes in oceanic halocarbon emissions, their atmospheric transport, and photochemistry.

1. Introduction

For the past few decades, atmospheric chemists have studied the ability of halogens to influence atmospheric composition, coastal air quality, and potentially climate. The high reactivity of atomic halogen radicals (e.g. Cl, Br, I, hereafter X) and halogen oxides (e.g. ClO, BrO, IO, hereafter XO) affects ozone and methane lifetimes in the atmosphere, exerting direct and indirect climatic radiative effects [Saiz-Lopez *et al.*, 2012; Hossaini *et al.*, 2015a]. Much research has been devoted to understand how halogen atoms released from anthropogenic long-lived halocarbons (LL) lead to the catalytic destruction of stratospheric ozone [Solomon, 1999]. However, a substantial portion of ozone depletion in the stratosphere depends on the natural emissions and transport of so-called halogenated very short-lived substances (VSLs) [Carpenter *et al.*, 2014], defined as trace gases whose chemical lifetimes are comparable to transport times in the troposphere (<0.5 years). These volatile halogenated VSLs are produced in biologically productive waters in tropical regions where strong vertical uplifts efficiently entrain near-surface air into the upper troposphere and lower stratosphere [e.g., Aschmann and Sinnhuber, 2013; Fernandez *et al.*, 2014; Liang *et al.*, 2014]. The additional bromine carried to the stratosphere by biogenic VSLs has been shown to influence stratospheric ozone photochemistry and trends [Hossaini *et al.*, 2015a; Sinnhuber and Meul, 2015], enhancing lowermost stratospheric ozone depletion as the additional BrO provides a reaction partner for ClO [Salawitch *et al.*, 2005].

Recent observational evidence shows that marine emissions of VSLs halocarbons can also exert a significant effect on tropospheric photochemistry [see Simpson *et al.*, 2015, and references therein]. VSLs photodecomposition products initiate a myriad of gas-phase and heterogeneous catalytic reactions that continuously change the relative partitioning between reactive and reservoir inorganic halogen species. There is a growing database of direct observations of reactive halogen compounds over the world's oceans, which have demonstrated their ubiquitous presence throughout the global background marine atmosphere [e.g., Read *et al.*, 2008; Lawler *et al.*, 2011; Prados-Roman *et al.*, 2015a], including the radiatively important middle to upper tropospheric region [Dorf *et al.*, 2008; Puentedura *et al.*, 2012; Dix *et al.*, 2013; Wang *et al.*, 2015]. Major efforts are underway to integrate these new data into global atmospheric models [e.g., von Glasow *et al.*, 2004; Yang *et al.*, 2005; Kerkweg *et al.*, 2008; Aschmann *et al.*, 2009; Hossaini *et al.*, 2010; Liang *et al.*, 2010; Ordóñez *et al.*, 2012; Parrella *et al.*, 2012]. The new results suggest that photochemical cycling of ocean-derived bromine and iodine can account for 15–30% of the overall catalytic ozone destruction throughout the tropospheric column [Saiz-Lopez *et al.*, 2012].

Most of the field experimental programs in the middle to upper troposphere have focused on the daytime measurement of halogen oxides, BrO and IO, which became the commonly targeted species for validating

and constraining model results [Dorf et al., 2008; Butz et al., 2009; Puenteadura et al., 2012; Dix et al., 2013; Wang et al., 2015]. However, recent global modeling studies have suggested that the combination of low ozone and cold conditions in the tropical tropopause layer (TTL) result in atomic bromine and iodine being the dominant daytime inorganic species upon decomposition of biogenic VSLs [Fernandez et al., 2014; Saiz-Lopez et al., 2014]. Here we describe the main causes that determine the natural appearance of the “tropical rings of atomic halogens,” where enhanced amounts of bare bromine and iodine atoms would globally circle around the Earth within the tropics following the Sun. The present study goes beyond the previously published work by providing a more detailed explanation of the photochemical drivers and kinetic factors that define the tropical rings, along with some potential atmospheric implications that the experimental confirmation of this hypothesized natural atmospheric phenomenon would imply.

2. Model Setup

We have used the global 3-D chemistry-climate model CAM-Chem (Community Atmospheric Model with Chemistry, version 4.0), configured with a horizontal resolution of 1.9° latitude by 2.5° longitude and 26 levels, from the surface up to ~40 km [Lamarque et al., 2012]. The model has been merged with a state-of-the-art tropospheric halogen chemistry scheme for chlorine, bromine, and iodine as described in detail in the works by Fernandez et al. [2014] and Saiz-Lopez et al. [2014]. Briefly, this includes geographically distributed and time-dependent emissions of nine VSLs chloro- (VSL^{Cl}), bromo- (VSL^{Br}), and iodo- (VSL^I) carbons (i.e., CHBr₃, CH₂Br₂, CH₂BrCl, CHBrCl₂, CHBr₂Cl, CH₃I, CH₂ICl, CH₂I₂, and CH₂I₂), which are released from the ocean to the atmosphere [Ordóñez et al., 2012]. Additionally, the model includes abiotic inorganic halogens that are also released within the marine boundary layer through heterogeneous sea-salt recycling [Fernandez et al., 2014] and O₃-mediated oxidation of aqueous iodide on the ocean surface [Prados-Roman et al., 2015b]. The tropospheric halogen chemical scheme includes 40 species and 150 gas-phase photochemical reactions with the most recent reaction rates and absorption cross sections given in JPL-2010 [Sander et al., 2011] and IUPAC-2008 [Atkinson et al., 2007, 2008]. Dry deposition, wet-scavenging, and ice-uptake processes for each individual species, as well as heterogeneous recycling reactions of inorganic halogen reservoirs, are also considered [Fernandez et al., 2014; Saiz-Lopez et al., 2014]. For the case of iodine, the scheme including the photochemistry of higher order iodine oxides from Saiz-Lopez et al. [2014] has been used here, although equivalent conclusions are obtained for the scheme without photolysis of higher iodine oxides.

3. Results and Discussion

All results shown here were computed considering only time-dependent output for noontime conditions at every grid point of the model (i.e., between 11:30 and 12:30 h local standard time). Tropical annual averages have been computed between 20°N and 20°S, while the tropical Western Pacific (TWP) warm pool area in February has been used as a representative region with strong vertical convection (0° ≤ latitude ≤ 20°N; 120°E ≤ longitude ≤ 165°E). In the absence of measurements of atomic bromine or iodine in the free and upper troposphere, our CAM-Chem halogen configuration has been validated with observed vertical profiles of the commonly targeted BrO [Dorf et al., 2008] and IO [Saiz-Lopez et al., 2015] radicals in the tropical atmosphere (see supporting information).

3.1. Tropical Rings of Atomic Halogens

Figure 1a shows a three-dimensional schematic representation of the modeled tropical rings of atomic bromine and iodine that surrounds the illuminated fraction of the Earth. Both rings are located approximately between 30°N and 30°S, with distinctive altitude intervals overlapping in depth: the atomic iodine ring is located between 11 and 17 km, just below the bromine ring (15 to 19 km), which expands well into the lowermost stratosphere. Within the rings, mixing ratios ranging from 0.15 to 2.80 pptv (annual mean of 1.3 at ~17 km) and from 0.05 to 1.20 pptv (annual mean of 0.6 pptv at ~14 km) are modeled for atomic Br and I, respectively (Figures 1c and 1d). The intensity and extent of the rings has a marked geographical and seasonal variability that depends on the distribution of oceanic sources and the background state of the atmosphere; with maximum concentrations located within regions of fast vertical uplift such as the TWP convective region (Figures S1 and S2). Thus, the proposed rings should be visualized as a couple of overlapped inhomogeneous layers that follow the daily solar cycle with variable mixing ratios at various longitudes, latitudes and altitudes (see Video S1 in the supporting information).

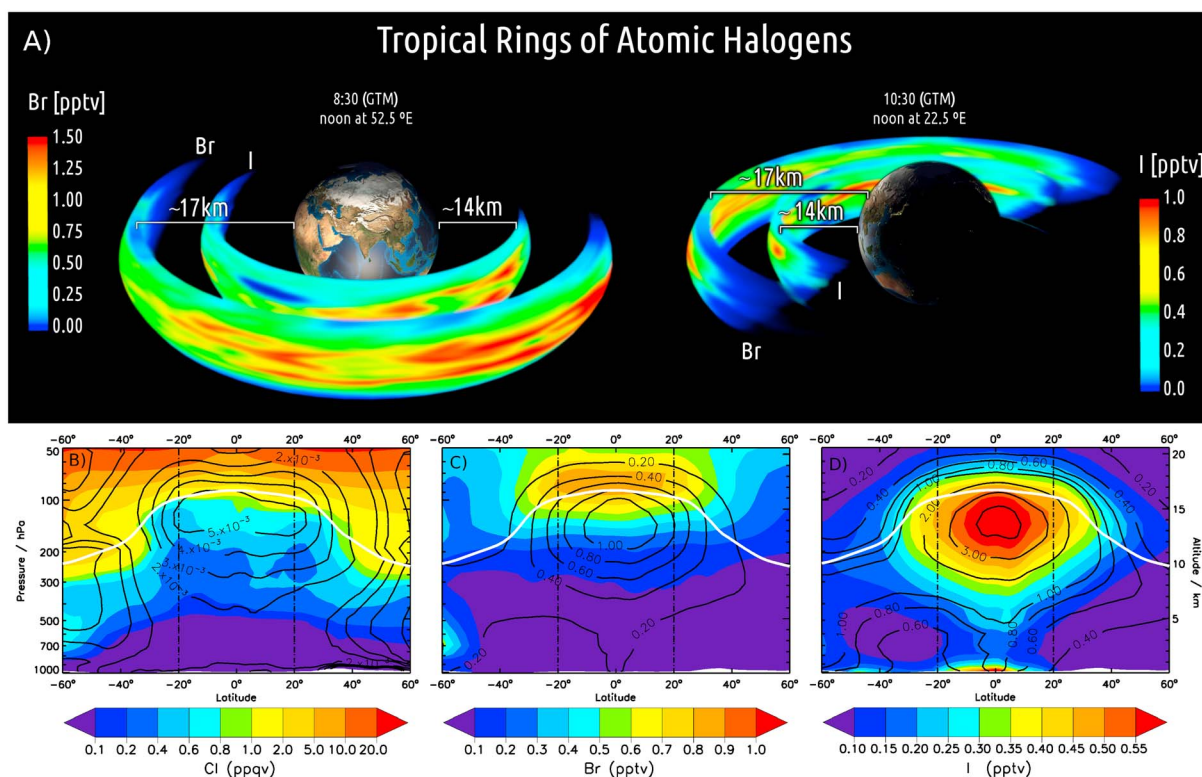


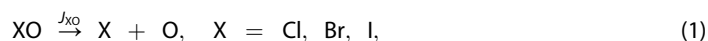
Figure 1. (a) Schematic representation of the “tropical rings of atomic halogens” at two different times of the day. Note that the Br and I rings should be superposed in height (11–17 km for iodine and 15–19 km for bromine) but have been intentionally separated to distinguish their different atomic vmr. (b–d) Annual daytime distributions of atomic halogens as a function of latitude and altitude for chlorine, bromine, and iodine, respectively. The black contour lines in the lower panels indicate the X/XO ratio for each family, while the white line shows the approximate location of the tropopause.

Within the rings, atomic bromine and iodine become the dominant inorganic halogen species for each family, particularly in the TTL (i.e., between ~12 and ~17 km; see *Fernandez et al.* [2014]). The main drivers of the halogen rings are the low ozone mixing ratios ($O_3 < 100$ ppbv) and cold temperatures ($T < 200$ K) prevailing in the upper tropical troposphere that slows down the otherwise dominant O_3 -mediated titration of the Br and I atoms released from VSLs photodissociation (see section 3.2). Our model results indicate that the ratio existent between the most abundant daytime reactive halogen species (i.e., Br/BrO and I/IO) is larger than unity within the TTL, just before stratospheric injection occurs. This is more evident in the TWP region where, in addition to the efficient convective uplift, the colder temperatures and lower ozone levels maximize the atomic halogen predominance within the TTL (see section 3.3 and Figures S1 and S2).

It is worth noting that even when a similar relative increase for chlorine atoms also exists in the upper troposphere (see supporting information), atomic Cl is a minor constituent throughout the whole troposphere with mixing ratios well below bromine and iodine levels (average $Cl < 1 \times 10^{-3}$ pptv = 1 ppqv, see Figure 1b). Although our model setup does not include other VSL^{Cl} sources such as CH_2Cl_2 and C_2Cl_4 [*Hossaini et al.*, 2015b] the tropical ring of atomic chlorine is not formed since atomic Cl never surpasses ClO mixing ratios. Note that the VSL^{Cl} species not included in this simulation only release a very small amount of reactive chlorine in the troposphere because they live long enough to be injected almost entirely as source gases to the stratosphere (see below).

3.2. Photochemical Drivers and Thermal Control

The atmospheric drivers controlling the formation of the tropical rings can be described considering the latitudinal (Figure 2) and vertical (Figure 3) variation of the main production and loss terms of halogen atoms in the atmosphere. The main production channel is the photolysis of halogen oxides



where J_{XO} is the photodissociation rate constant of each halogen oxide species in s^{-1} (Figures 2a and 2d and

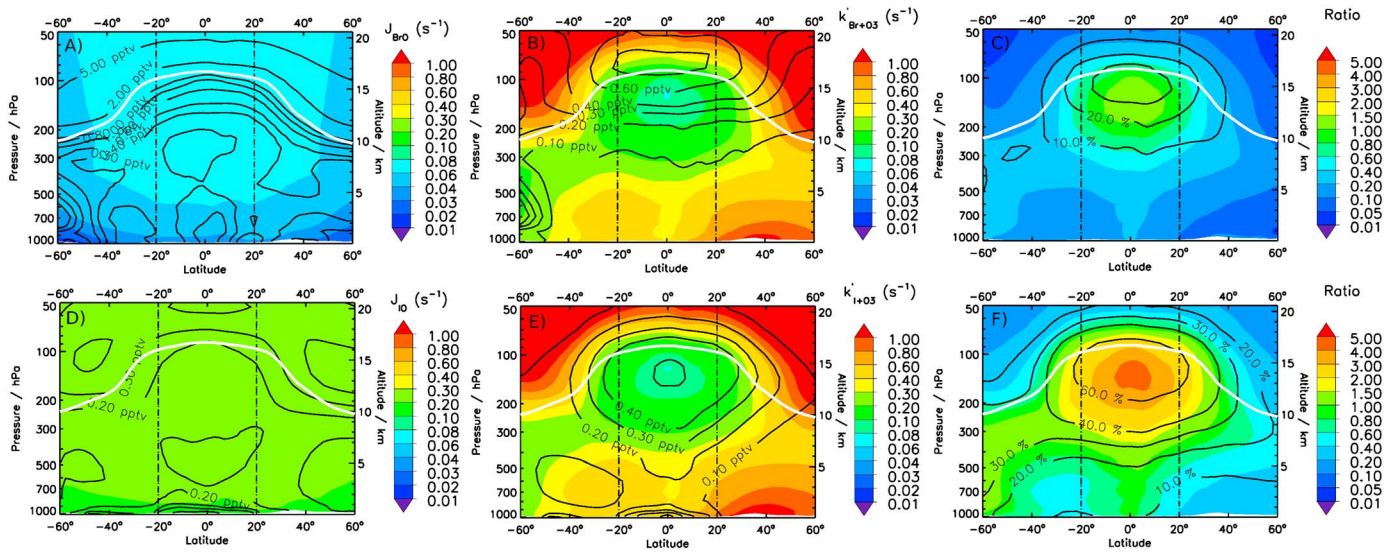
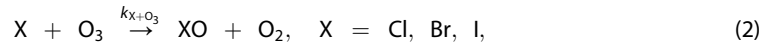


Figure 2. Annual zonal averages of the main drivers determining the formation of the tropical ring of (a–c) atomic bromine and (d–f) iodine: (a, d) Photodissociation production term (J_{XO} , color contours) and halogen oxide mixing ratio (black lines); (b, e) Pseudo first-order loss rate term (k'_{X+O_3} , color contours) and atomic halogen mixing ratio (black lines); (c, f) X/XO ratio (color contours) and atomic halogen percentage abundance (black lines). The white line indicates the approximate location of the tropopause.

filled symbols in Figures 3a and 3b). Once produced, halogen atoms rapidly react with ozone, cycling back to the halogen oxide through

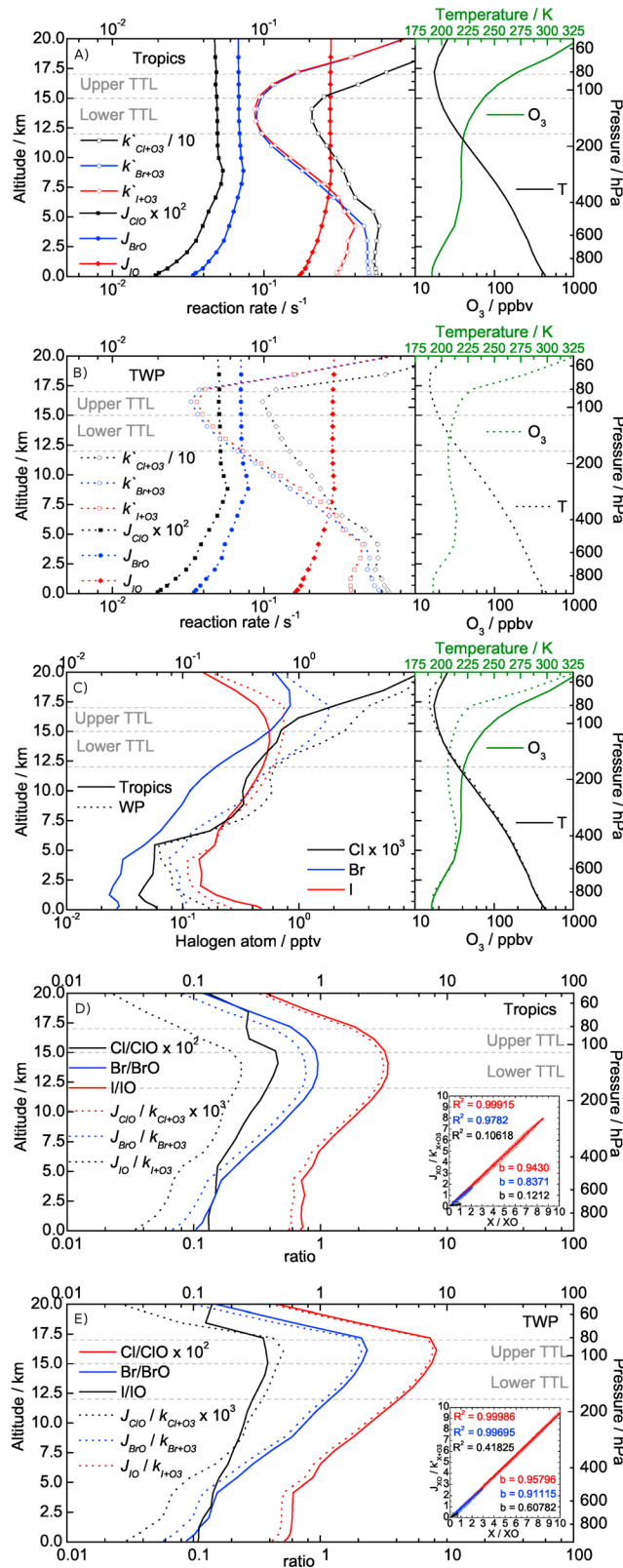


where k_{X+O_3} is the second-order rate constant in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. Considering the prevailing ozone distributions in the atmosphere (Figure S3), the loss term can be approximated by the pseudo first-order reaction rate $k'_{X+O_3} = k_{X+O_3} \times [O_3]$ in seconds. Notably, the k'_{X+O_3} loss term shows a pronounced decrease in the upper troposphere following the temperature and ozone profiles, with minimum values occurring in the upper TTL (Figures 2b and 2e and empty symbols in Figures 3a and 3b). This characteristic vertical dependence can be explained considering the general Arrhenius expressions for the second-order rate constants for each halogen family

$$k_X = A_X \times e^{\left(-\frac{E_X/R}{T}\right)}, \quad X = Cl, Br, I, \quad (3)$$

where A is the Arrhenius factor and E/R is the activation energy for each reaction [Sander et al., 2011]. As the ozone reaction with all of the halogen atoms have positive activation energies (Table S1), the overall rate constants decrease as the temperature decreases, reaching a local minimum within the TTL.

An additional factor influencing the maximum abundance and height thickness of each tropical ring is the different photolysis efficiencies of organic VSLs (J_{VSLs}) species [Ordóñez et al., 2012]; i.e., the photolytic lifetime of VSL^I (hours to days) are much shorter than those for VSL^{Br} and VSL^{Cl} (weeks to months). Thus, the atmospheric partitioning between organic halogens (i.e., carbon-bonded VSLs and LL source gases) and their inorganic decomposition products (X_y) is very different for each family (Figure 4). For instance, more than 90% of VSL^I is in the form of I_y , while due to the dominant contribution of LL sources (such as Halons and CFCs with lifetimes > 1 year), Br_y and Cl_y percentages represent at most 15% and 0.5% of the total (organic + inorganic) bromine and chlorine loading in the troposphere, respectively. Note, however, that J_{VSLs} constitute a net source of inorganic halogens, while J_{XO} represents only a change in partitioning between different reactive halogen species (i.e., X and XO) within the inorganic fraction. Other reactions transforming reactive halogen atoms into inorganic reservoirs are the losses through $X + CH_2O$, $X + HO_2$, and $X + NO_2 + M$, which added together represent at most 0.1%, 2%, and 15% of the dominant $X + O_3$ channel for iodine, bromine, and chlorine, respectively. In addition, the halogen nitrates formation through $XO + NO_2 + M \rightarrow XONO_2$ represents only ~0.5% (iodine) and ~2% (bromine) of the correspondent J_{XO} competing channel, while $ClONO_2$ formation is at least 2 orders of magnitude larger than the ClO photolysis within the free and upper troposphere. Moreover, the initiation step in the halogen-mediated methane oxidation proceeds only for



chlorine (i.e., $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$), as the equivalent reaction for bromine and iodine is very slow [Lary and Toumi, 1997; Sander et al., 2011]. This leads to the fraction of reactive chlorine ($\text{Cl} + \text{ClO}$) converted to reservoir species (mostly HCl and ClONO_2) to be much larger than that for bromine and iodine (see top axis in Figure 4).

Thus, the height where bare halogen atoms are the dominant species is determined by the crossing point between J_{XO} and $k'_{\text{X}+\text{O}_3}$ channels (Figure 3), but the maximum atomic Br and I mixing ratios within the rings depend on the balance between the J_{VSLs} sources releasing halogen atoms, the relative abundance of reactive species respect to inorganic reservoirs $[(\text{X} + \text{XO})/\text{X}_i]$, and the net sinks of reservoir inorganic species through washout, aerosol scavenging, and ice uptake [Fernandez et al., 2014; Saiz-Lopez et al., 2014]. Notably, sensitivity analysis showed that within the tropical rings, atomic bromine and iodine would dominate the daytime inorganic partitioning regardless of the total inorganic halogen burden (e.g., considering only major or minor VSL^{Br} sources [Fernandez et al., 2014], under different washout regimes, or allowing/neglecting the photolysis of higher iodine oxides [Saiz-Lopez et al., 2014]).

Figure 3. Vertical profiles of the main drivers defining the height and thickness of the rings. Black, blue, and red lines indicate chlorine, bromine, and iodine, respectively. (a) Annual production terms (filled symbols) and loss channels (empty symbols) within the tropics. The right panels show the corresponding vertical ozone and temperature profiles; (b) Idem Figure 3a but for the TWP in February; (c) Atomic halogen mixing ratio profile for the tropics (solid) and the TWP (dotted); (d) X/XO ratio (solid lines) and the approximate steady state ratio $J_{\text{XO}}/k'_{\text{X}+\text{O}_3}$, dotted lines) within the Tropics. The inset graph shows the linear correlation between X/XO and $J_{\text{XO}}/k'_{\text{X}+\text{O}_3}$; (e) Idem Figure 3d but for the TWP in February. Note that the profiles for chlorine have been scaled by a multiplicative factor.

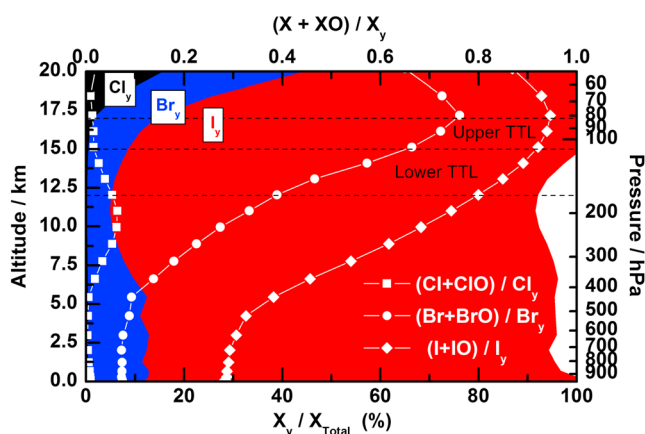


Figure 4. Annual tropical vertical profiles of the percentage of inorganic halogen (X_y) mixing ratio respect to the total (organic + inorganic) halogens loading for each family (X_y/X_{Total} , colored areas, bottom axis). The corresponding fraction of reactive halogen ($X + XO$) within the inorganic portion is shown by filled symbols on the top axis.

3.3. The Halogen Ratio and Its T/O_3 Dependence Within the Tropics

Equations (1) and (2) establish a daytime photochemical steady state, which can be expressed as

$$\frac{[X]}{[XO]} = \frac{J_{XO}}{k_{X+O_3}[O_3]} = \frac{J_{XO}}{k'_{X+O_3}}, \quad X = Cl, Br, I. \quad (4)$$

Then, the relative abundance of Cl, Br, and I atoms (respect to ClO, BrO, and IO, respectively) depends on the ratio existent between the photodissociation of the halogen oxide and its pseudo first-order reaction rate, which in turn depends on ozone and temperature through equation (3). The zonal average distributions of J_{BrO} and J_{IO} shown in Figures 2a and 2d remain practically constant with altitude and latitude, while the thermal-kinetic k'_{X+O_3} loss term follows the shape of the temperature and ozone profiles (Figures 2b and 2e), reducing the formation of the BrO and IO oxides within the TTL. Thus, the X/XO ratio for bromine and iodine is greater than unity within the TTL.

This simple kinetic control, altogether with the different photolytic efficiency of the halogen oxides ($J_{IO} > J_{BrO} > J_{ClO}$) determines the extent and intensity of the bromine and iodine ratios (see Figures 3d and 3e). Even when both bromine and iodine have large activation energies (i.e., the Arrhenius profile for both losses terms are similar), the fastest photolytic efficiency of iodine oxide results in the I/IO ratio being the largest of the three halogen families. On the other side, even though a similar vertical profile for the chlorine ratio is observed, $Cl/ClO < 1$ because the photolytic efficiency of ClO is at least 3 orders of magnitude smaller than the $Cl + O_3$ reaction (see Figure S4). Despite the underestimation of total VSL^{Cl} in the current setup, our model annual average Cl_y levels in the upper TTL are ~ 50 pptv in agreement with recent studies [Hossaini et al., 2015b]. Thus, in contrast to bromine and iodine, reservoir species dominates the inorganic chlorine partitioning and the $(Cl + ClO)/Cl_y$ ratio is smaller than 0.01 throughout the whole troposphere (see Figure 4).

The excellent correlation between the left- and right-hand terms of equation (4) shown in the inset of Figures 3d and 3e indicates that the steady state for the iodine and bromine families can be fully represented by considering only J_{XO} and k'_{X+O_3} . The poor fit of the Cl/ClO ratio to equation (4) indicates, however, that additional production and loss channels for Cl atoms and the ClO radical, besides those given by equations (1) and (2), must be considered. Indeed, the rapid $Cl + CH_4$, $Cl + C_2H_6$ and $Cl + CH_2O$ reactions (all of them yielding gas-phase HCl) compete with the $Cl + O_3$ reaction in the troposphere, while the $ClO + NO_2$ reaction converts most of the reactive chlorine into less reactive reservoirs (e.g., $ClONO_2$) instead of releasing Cl through J_{ClO} [Simpson et al., 2015].

3.4. Atmospheric Implications

The “tropical rings of atomic halogens” link a wide range of interrelated atmospheric implications: First, it provides insights on how the degradation products of biogenic VSLs interact with the upper troposphere on their way up to the stratosphere. Because all halogen oxide observations in this region of the atmosphere were made during the day [Dorf et al., 2008; Butz et al., 2009; Puente-dura et al., 2012; Dix et al., 2013;

Wang *et al.*, 2015], most of the atmospheric bromine and iodine in and near the tropopause could be hidden as atomic Br and I, instead of the commonly targeted BrO and IO radicals. The field confirmation of the tropical rings would indicate that a considerable portion of the oceanic VSLs supply is already in its inorganic reactive form (i.e., capable of catalytically destroy ozone) before reaching the lowermost stratosphere [Salawitch *et al.*, 2005]. This highlights the importance of performing field campaigns to confirm the prevailing existence of atomic halogen species within the TTL, as they would be a very valuable proxy for constraining product gas injection of ozone depleting substances in chemistry-climate models. Our model results indicate that up to 90% (60%) of the total daytime inorganic iodine (bromine) burden could be hidden as bare I (Br) atoms in regions of the TTL with strong convective transport such as the TWP during February. Second, the bromine ring would also play a fundamental role in the production of oxidized mercury (Hg(II)) species occurring in the middle and upper troposphere [Holmes *et al.*, 2006], which is critical to assess the global deposition and accumulation of this toxic element in marine ecosystems. Within the ring, atomic Br concentrations are high and ambient temperature is low, increasing the formation of the Hg(I)-Br intermediate species while suppressing its thermal decomposition during the oxidation process. Following equation (2) from Parrella *et al.* [2012], we estimated that at least 60% of the overall Hg(II) oxidation occurs in the upper troposphere, of which approximately one third takes place within the tropical ring of atomic bromine (see Table S2). Compared to the mass-weighted global lifetime for mercury oxidation ($\tau_{\text{global}} \approx 172$ days), the lifetime inside the tropical ring is ~ 96 days, with minimum values occurring coincidentally with the largest Br mixing ratios. Indeed, observations have identified the presence of Br and I atoms invariably associated with mercury in aerosols sampled at the tropical tropopause [Murphy *et al.*, 2006]. Third, the atomic iodine ring, which extends up to ~ 17 km, is linked to the recent suggestion that present day stratospheric injection of inorganic iodine could be as much as 5 times larger than the last World Meteorological Organization recommendation [Saiz-Lopez *et al.*, 2015], with a potential ozone depletion impact in the lowermost stratosphere comparable to, or even larger than, that for VSL^{Br}. Indeed, up to 80% of daytime I_y can be in the form of atomic iodine at the coldest point tropopause (~ 17 km). Fourth, the atomic I ring could also be indicative of the important role that iodine chemistry plays in the oxidative capacity of the pristine and polluted troposphere, as the iodine-mediated ozone catalytic cycles are much more efficient than those for bromine and chlorine radicals. This is in line with the recent suggestion of a negative feedback between anthropogenic ozone and natural iodine emissions from the sea surface, which represent a geochemical feedback loop by which current ocean emissions of iodine act as a natural buffer for ozone pollution and its radiative forcing in the global marine environment [Prados-Roman *et al.*, 2015b].

4. Concluding Remarks

Current preindustrial to 21st century projections of tropospheric ozone (considering only long-lived halogens) revealed large discrepancies between observed and modeled ozone abundances in the tropical upper troposphere [Young *et al.*, 2013] and highlighted the importance of performing rigorous investigations of additional factors driving the budget of tropical upper tropospheric ozone, including the role of natural halogenated VSLs. This study suggests that to properly constrain the halogen budget in the present and future tropical tropopause, experimental programs should include a strategy for the measurement of atomic halogens. If the emission and atmospheric transport of biogenic VSLs is found to be sensitive to climatically driven changes in the state of the world's oceans (through changes in atmospheric winds, sea surface temperature, upwelling, and/or nutrient supply), then the extent and intensity of the halogen rings would directly respond to such geophysical changes. Thus, if the "tropical rings of atomic halogens" are experimentally confirmed, a potentially important new link between oceanic halocarbons emissions, atmospheric photochemistry, ozone, and temperature would have been found.

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Acknowledgments

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