Iodine chemistry in the troposphere and its effect on ozone

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Abstract. Despite the potential influence of iodine chemistry on the oxidizing capacity of the troposphere, reactive iodine distributions and their impact on tropospheric ozone remain almost unexplored aspects of the global atmosphere. Here we present a comprehensive global modelling experiment aimed at estimating lower and upper limits of the inorganic iodine burden and its impact on tropospheric ozone. Two sets of simulations without and with the photolysis of I₂O₂ oxides (i.e. I₂O₂, I₂O₃ and I₂O₄) were conducted to define the range of inorganic iodine loading, partitioning and impact in the troposphere. Our results show that the most abundant daytime iodine species throughout the middle to upper troposphere is atomic iodine, with an annual average tropical abundance of (0.15–0.55) pptv. We propose the existence of a “tropical ring of atomic iodine” that peaks in the tropical upper troposphere (∼11–14 km) at the equator and extends to the sub-tropics (30° N–30° S). Annual average daytime I / IO ratios larger than 3 are modelled within the tropics, reaching ratios up to ∼20 during vigorous uplift events within strong convective regions. We calculate that the integrated contribution of catalytic iodine reactions to the total rate of tropospheric ozone loss (IOₓ Loss) is 2–5 times larger than the combined bromine and chlorine cycles. When I₂O₂ photolysis is included, IOₓ Loss represents an upper limit of approximately 27, 14 and 27 % of the tropical annual ozone loss for the marine boundary layer (MBL), free troposphere (FT) and upper troposphere (UT), respectively, while the lower limit throughout the tropical troposphere is ∼9 %. Our results indicate that iodine is the second strongest ozone-depleting family throughout the global marine UT and in the tropical MBL.

We suggest that (i) iodine sources and its chemistry need to be included in global tropospheric chemistry models, (ii) experimental programs designed to quantify the iodine budget in the troposphere should include a strategy for the measurement of atomic I, and (iii) laboratory programs are needed to characterize the photochemistry of higher iodine oxides to determine their atmospheric fate since they can potentially dominate halogen-catalysed ozone destruction in the troposphere.

1 Introduction

The oceans provide the main source of iodine to the atmosphere. Methyl iodide (CH₃I) and other very short-lived (VSL) iodocarbons (e.g. CH₂I₂, C₂H₅I, C₃H₇I, CH₂ICl, CH₂IBr) are produced by biotic and photochemical processes, and released to the atmosphere from supersaturated ocean waters (Carpenter et al., 2012; Saiz-Lopez et al., 2012a). Laboratory studies have also established the gaseous emission of molecular iodine (I₂) following the reaction of aqueous iodide with atmospheric ozone at the sea surface (Garland and Curtis, 1981; Sakamoto et al., 2009; Hayase et al., 2010). More recently, it has been shown that HOI is the major species emitted as a result of this oxidative reaction (Carpenter et al., 2013; MacDonald et al., 2014). Several modelling studies and analysis of experimental data have suggested that the HOI / I₂ additional inorganic source must surpass the emission strength of organic VSL iodocarbons in order to reproduce observed iodine monoxide (IO) measure-
Table 1. Iodine chemistry scheme in CAM-Chem: Bimolecular, thermal decomposition and termolecular reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>I + O₃ → IO + O₂</td>
<td>2.1 × 10⁻¹¹ exp(−830/T)</td>
<td>1</td>
</tr>
<tr>
<td>IO + O₃ → OIO + O₂</td>
<td>3.6 × 10⁻¹⁶</td>
<td>2</td>
</tr>
<tr>
<td>I + HO₂ → HI + O₂</td>
<td>1.5 × 10⁻¹¹ exp(−1090/T)</td>
<td>3</td>
</tr>
<tr>
<td>IO + NO → I + NO₂</td>
<td>7.15 × 10⁻¹² exp(300/T)</td>
<td>1</td>
</tr>
<tr>
<td>IO + HO₂ → HOI + O₂</td>
<td>1.4 × 10⁻¹¹ exp(540/T)</td>
<td>1</td>
</tr>
<tr>
<td>IO + IO → OIO + I</td>
<td>2.13 × 10⁻¹¹ exp(180/T) × [1 + exp(−p/191/42)]</td>
<td>1, 4</td>
</tr>
<tr>
<td>IO + IO → I₂O₂</td>
<td>3.27 × 10⁻¹¹ exp(180/T) × [1 − 0.65 exp(−p/191/42)]</td>
<td>1, 4</td>
</tr>
<tr>
<td>IO + OIO → I₂O₃</td>
<td>w₁ × (w₂ · T)⁰</td>
<td>4, 5, 6⁸</td>
</tr>
<tr>
<td>OIO + OIO → I₂O₄</td>
<td>w₁ × (w₂ · T)⁰</td>
<td>4, 5, 6⁸</td>
</tr>
<tr>
<td>I₂ + O → IO + I</td>
<td>1.25 × 10⁻¹⁰</td>
<td>1</td>
</tr>
<tr>
<td>IO + O → I + O₂</td>
<td>1.4 × 10⁻¹⁰</td>
<td>1</td>
</tr>
<tr>
<td>IO + OH → HO₂ + I</td>
<td>1.0 × 10⁻¹⁰</td>
<td>7</td>
</tr>
<tr>
<td>I₂O₂ → OIO + I</td>
<td>w₁ × (w₂ / T)⁹</td>
<td>5, 6, 8⁸</td>
</tr>
<tr>
<td>I₂O₂ → IO + IO</td>
<td>w₁ × (w₂ / T)⁹</td>
<td>5, 6, 8⁸</td>
</tr>
<tr>
<td>I₂O₄ → 2 OIO</td>
<td>w₁ × (w₂ / T)⁹</td>
<td>5, 8⁸</td>
</tr>
<tr>
<td>I₂ + OH → HOI + I</td>
<td>1.8 × 10⁻¹⁰</td>
<td>3</td>
</tr>
<tr>
<td>I₂ + NO₃ → I + IONO₂</td>
<td>1.5 × 10⁻¹²</td>
<td>9</td>
</tr>
<tr>
<td>I + NO₃ → IO + NO₂</td>
<td>1.0 × 10⁻¹⁰</td>
<td>1</td>
</tr>
<tr>
<td>OH + HI → I + H₂O</td>
<td>1.6 × 10⁻¹¹ exp(440/T)</td>
<td>1</td>
</tr>
<tr>
<td>I + IONO₂ → I₂ + NO₃</td>
<td>9.1 × 10⁻¹¹ exp(−146/T)</td>
<td>5</td>
</tr>
<tr>
<td>HOI + OH → IO + H₂O</td>
<td>2.0 × 10⁻¹⁵</td>
<td>10</td>
</tr>
<tr>
<td>IO + DMS → DMSO + I</td>
<td>3.2 × 10⁻¹⁳ exp(−925/T)</td>
<td>11</td>
</tr>
<tr>
<td>IONO₂ → I + NO₂</td>
<td>1008 × 10¹⁵ exp(−13670/T)</td>
<td>12, 13, 14</td>
</tr>
<tr>
<td>IONO₂ → IO + NO₂</td>
<td>w₁ × (w₂ / T)⁹</td>
<td>5, 15</td>
</tr>
<tr>
<td>INO +INO → I₂ + 2NO</td>
<td>8.4 × 10⁻¹¹ exp(−2620/T)</td>
<td>3</td>
</tr>
<tr>
<td>INO₂ + INO₂ → I₂ + 2NO₂</td>
<td>4.7 × 10⁻¹³ exp(−1670/T)</td>
<td>1</td>
</tr>
<tr>
<td>OIO + NO → IO + NO₂</td>
<td>1.1 × 10⁻¹² exp(542/T)</td>
<td>14</td>
</tr>
<tr>
<td>HI + NO₃ → I + HNO₃</td>
<td>1.3 × 10⁻¹² exp(−1830/T)</td>
<td>16</td>
</tr>
<tr>
<td>IO + BrO → Br + I + O₂</td>
<td>0.30 × 10⁻¹¹ exp(510/T)</td>
<td>1</td>
</tr>
<tr>
<td>IO + BrO → Br + OIO</td>
<td>1.20 × 10⁻¹¹ exp(510/T)</td>
<td>1</td>
</tr>
<tr>
<td>I + BrO → IO + Br</td>
<td>1.44 × 10⁻¹¹ exp(−17)</td>
<td>17, 18, 19</td>
</tr>
<tr>
<td>IO + ClO → I + OCIO</td>
<td>2.585 × 10⁻¹² exp(280/T)</td>
<td>1</td>
</tr>
<tr>
<td>IO + ClO → I + Cl + O₂</td>
<td>1.175 × 10⁻¹² exp(280/T)</td>
<td>1</td>
</tr>
<tr>
<td>IO + ClO → ClO + O₂</td>
<td>0.940 × 10⁻¹² exp(280/T)</td>
<td>1</td>
</tr>
<tr>
<td>IO + Br → I + BrO</td>
<td>2.49 × 10⁻¹¹</td>
<td>18, 19</td>
</tr>
<tr>
<td>IO + NO₃ → OIO + NO₂</td>
<td>9.0 × 10⁻¹²</td>
<td>20</td>
</tr>
<tr>
<td>IO + CH₃O₂ → CH₂O + I + HO₂</td>
<td>2.0 × 10⁻¹²</td>
<td>2h</td>
</tr>
</tbody>
</table>

Early pioneering work by Chameides and Davis (1980) and Solomon et al. (1994) showed that both organic and inorganic iodine compounds photo-dissociate rapidly in the troposphere to release iodine atoms, which then react mainly with ozone to generate IO. A steady state is then established between I and IO as a result of the fast photolysis of the oxide, and therefore the two species are termed collectively as reactive iodine, or IOₓ = 1 + IO. The IOₓ react further with other species to generate different forms of inorganic iodine (Saiz-Lopez et al., 2012a, see Table 1). The atmospheric chemical processing of iodine species influences the oxidizing capacity of the troposphere through catalytic ozone-depleting cycles (IOₓ Loss, i.e. Chameides and Davis, 1980; Solomon et al., 1994; Davis et al., 1996; Vogt et al., 1999; McFiggans et al., 2000; Brasseur and Solomon, 2005) and changes to the HOₓ (i.e. [HO₂]/[OH]) and NOₓ (i.e. [NO₂]/[NO]) ratios (Bloss et al., 2005). It also makes a negative contribution to the radiative flux in the tropical troposphere (Saiz-Lopez et al., 2012b), and produces higher-order iodine oxides (IₓOₙ) which have been proposed to participate in the formation of ultrafine aerosol particles in coastal environments (Hoffmann et al., 2001; O’Dowd et al., 2002; Jimenez et al., 2003; McFiggans et al., 2004, 2010; Pechtl et
Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_{cm^{-3}}$ molecule$^{-1}$ s$^{-1}$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$I + OH $\rightarrow$ I + H$_2$O + HO$_2$</td>
<td>$2.90 \times 10^{-12}$ e$^{-(-1100/T)}$</td>
<td>3</td>
</tr>
<tr>
<td>I + NO$_2$ (+ M) $\rightarrow$ INO$_2$ (+ M)</td>
<td>$k_0 = 3 \times 10^{-31} (T/300)^{-1}$</td>
<td>3$^1$</td>
</tr>
<tr>
<td>IO + NO$_2$ (+ M) $\rightarrow$ IONO$_2$ (+ M)</td>
<td>$k_0 = 6.5 \times 10^{-31} (T/300)^{-3.5}$</td>
<td>3$^1$</td>
</tr>
<tr>
<td>I + NO (+ M) $\rightarrow$ INO (+ M)</td>
<td>$k_0 = 1.8 \times 10^{-32} (T/300)^{-1}$</td>
<td>3$^1$</td>
</tr>
<tr>
<td>OIO + OH (+ M) $\rightarrow$ HOIO$_2$ (+ M)</td>
<td>$k_0 = 1.5 \times 10^{-27} (T/300)^{-3.93}$</td>
<td>14$^1$</td>
</tr>
</tbody>
</table>

$^1$ IPCC-2008 (Atkinson et al., 2007); $^2$ Dillon et al., 2006b; $^3$ JPL-2010 (Sander et al., 2011); $^4$ Gómez Martín et al., 2007; $^5$ Kaltsoyannis and Plane, 2008; $^6$ Gómez Martín et al., 2013; $^7$ Bisch et al., 2007; $^8$ Gómez Martín and Plane, 2009; $^9$ Chambers et al., 1992; $^{10}$ Chameides and Davis, 1980; $^{11}$ Dillon et al., 2006b; $^{12}$ McFiggans et al., 2000; $^{13}$ Jenkin et al., 1985; $^{14}$ Plane et al., 2006; $^{15}$ Allan and Plane, 2002; $^{16}$ Lascar et al., 1991; $^{17}$ Laszlo et al., 1997; $^{18}$ Bedjanian et al., 1997; $^{19}$ Gilles et al., 1997; $^{20}$ Dillon et al., 2008.

Different techniques have enabled measurements of tropospheric iodine species in geographical locations ranging from the tropical troposphere to the polar boundary layer (Saiz-Lopez and von Glasow, 2012). Comprehensive reports and inventories of organic VSL iodocarbons across the world oceans have been published in the last decades (Saiz-Lopez et al., 2012a, and references therein). Inorganic reactive iodine species have been observed in the marine boundary layer (MBL) well above their detection limits, including IO (Alicke et al., 1999), OIO (Allan et al., 2000), I$_2$ (Saiz-Lopez and Plane, 2004), and I (Bale et al., 2008). More recently, the detection of IO in the sub-tropical (Puenteudera et al., 2012) and tropical (Dix et al., 2013) free troposphere shows a widespread presence of active iodine species throughout the marine troposphere.

Based on iodine’s faster catalytic ozone-depletion kinetics compared to that of bromine and chlorine, box- and one-/two-dimensional (Solomon et al., 1994; Davis et al., 1996; Vogt et al., 1999; Calvert and Lindberg, 2004; Saiz-Lopez et al., 2007; Sommariva and von Glasow, 2012; Sommariva et al., 2012) and global (Saiz-Lopez et al., 2012b) modelling studies have suggested the potential important role of iodine in the destruction of tropospheric ozone. Additionally, recent studies have pointed out differences between observed and modelled O$_3$ abundances in the tropical upper troposphere (Young et al., 2013) and northern mid-latitude lower
troposphere (Parrish et al., 2014), and highlighted the importance of performing a rigorous investigation of additional factors driving the budget of tropospheric ozone. Following the evidence of the ubiquitous presence of reactive iodine in the troposphere, we present simulations with a chemistry-climate model that includes geographically distributed VSL iodocarbon sources (CH$_3$I, CH$_3$I$_2$, CH$_2$ICl and CH$_2$IBr) as well as global inorganic iodine emissions (HOI / I$_2$) from the oceans. The model includes a state-of-the-art iodine chemistry scheme considering I$_2$O$_y$ and their photolytic and thermal decomposition, individualized wet-removal processes and ice-uptake, as well as heterogeneous recycling reactions over sea-salt aerosol and ice particles. Here we highlight, for the first time in a global model, some of the unique aspects of iodine chemistry that drive the partitioning of organic and inorganic iodine species throughout the troposphere. The I$_2$O$_y$ represent a substantial mass of atmospheric iodine currently unaccounted for and subject to a large degree of uncertainty. The upper and lower limits of the tropospheric iodine burden are shown to be strongly dependent on the uncertainties related to the chemical fate of I$_2$O$_y$ species, whose photochemistry and reactivity represent a fundamental problem in our current knowledge of iodine chemistry and its effects in the atmosphere. Based on our results, we discuss implications for the transport and partitioning of iodine species to the free troposphere (FT) and upper troposphere (UT), and assess its relevance on the tropospheric ozone budget.

2 Model description: CAM-Chem setup

The global 3-D chemistry climate model CAM-Chem (Community Atmospheric Model with Chemistry, version 4.0), included into the CESM framework (Community Earth System Model, version 1.1.1) was used for this study (Lamarque et al., 2012). CAM-Chem can be configured at different grid resolutions and dynamical configurations. The setup used here considers a horizontal grid resolution of 1.9° (latitude) × 2.5° (longitude) and 26 hybrid vertical levels from the surface to approximately 40 km. CAM-Chem has the capability to perform simulations using specified dynamics (SD), where offline meteorological fields are used to compute the atmospheric transport. In order to eliminate dynamical alterations between simulations with dissimilar chemical mechanisms, we performed all simulations in SD mode, considering the same high-frequency meteorological input from a previous CAM-Chem 15-year simulation without halogen chemistry. In this way, our CAM-Chem setup implies that we force the system to evolve as if it was a CTM (chemical transport model), in a manner that the chemical changes existent at different locations and altitudes between a set of independent simulations can be directly addressed. See Lamarque et al. (2012) for a complete description of the SD setup.

The development of the benchmark CAM-Chem mechanism is based on MOZART-4 (Emmons et al., 2010). For this configuration, an improved representation of stratospheric chemistry, considering heterogeneous processes in polar clouds from MOZART-3 (Kinnison et al., 2007; Wegner et al., 2013), has also been used. The chemical solver is initialized with identical chemical boundary conditions for any given species in all simulations presented here, and all the atmospheric oxidants are computed online at all times (i.e. without considering prescribed monthly OH fields as done in previous studies). Our current setup includes an organic and inorganic halogen (chlorine, bromine and iodine) photochemistry mechanism, considering both natural and anthropogenic sources, heterogeneous recycling, dry and wet deposition – both in the troposphere and lower stratosphere (Ordóñez et al., 2012; Fernandez et al., 2014). For iodine species we have compiled a state-of-the-art chemical scheme as described below.

2.1 Atmospheric chemistry of iodine

The chemistry of chlorine and bromine VSL species in CAM-Chem has been described in detail previously (Ordóñez et al., 2012; Fernandez et al., 2014). In this work we have used the same emissions inventory of bromo- (CHBr$_3$, CH$_2$Br$_2$, CH$_3$BrCl, CHBr$_2$Cl and CHBrCl$_2$) and iodocarbons presented there, extending the iodine inorganic chemistry mechanism. VSL oceanic sources of CH$_2$I, CH$_2$ICl and CH$_2$IBr are based on parametrizations of chlorophyll-a satellite maps, including latitudinal variations between 50° N–50° S, a time-dependent ice-mask for polar oceans and a monthly seasonality (see Ordóñez et al. (2012) for details). The global CH$_3$I (with X = Cl, Br or I) flux in the model is ∼437 Gg yr$^{-1}$. CH$_3$I emissions are taken from
an existing top-down inventory (Bell et al., 2002), which included major oceanic sources (213 Gg yr\(^{-1}\)) as well as some land-based fluxes from rice paddies, wetlands, biofuel and biomass burning (91 Gg yr\(^{-1}\)), yielding a global CH\(_3\)I flux of 304 Gg yr\(^{-1}\). For the emissions of most VSL iodocarbons we follow a solar diurnal profile, with emissions peak in the early afternoon and null emissions at night. The exception is CH\(_2\)I\(_2\) which showed an improved agreement with measurements when ~1/4 of the total emissions occurs during the night (Ordóñez et al., 2012). In addition, inorganic iodine oceanic sources have been included in the lowest layer of the model (~150 m depth), based on recent laboratory studies that determined the abiotic gaseous emission of HOI and I\(_2\) following the oxidation of aqueous iodide by atmospheric ozone on the ocean surface (Carpenter et al., 2013; MacDonald et al., 2014). The global modelled emissions of HOI/I\(_2\) account for ~1.9 Tg (I) yr\(^{-1}\) and depend on the deposition of tropospheric ozone to the ocean surface, the sea surface temperature and the wind speed (see Prados-Roman et al. (2014) for further details on the implementation of the inorganic iodine source). This additional inorganic source is somewhat larger than the ~1.2 Tg (I) yr\(^{-1}\) value of Saiz-Lopez et al. (2012b) and within the range of values required to reconcile IO measurements in the MBL at coastal sites (i.e. in the range of (10−70) × 10\(^7\) atoms (I) cm\(^{-2}\) s\(^{-1}\); see Mahajan et al. (2010); Großmann et al. (2013) and references therein). The computed lifetimes of CH\(_2\)ICl, CH\(_2\)Br and CH\(_2\)I\(_2\) range from minutes to hours in agreement with previous studies (Rattigan et al., 1997; Roehl et al., 1997; Mössinger et al., 1998), while for CH\(_3\)I it is in the order of 5−8 days (Rattigan et al., 1997; Roehl et al., 1997).

Table 1 presents the bimolecular, thermal decomposition and termolecular reactions of iodine species included in the chemical mechanism. Updates with respect to previous analyses (Ordóñez et al., 2012; Saiz-Lopez et al., 2012b) are mainly based on theoretical studies on the formation, photochemistry and thermal decomposition of higher iodine oxides, collectively called I\(_x\)O\(_y\) (Gómez Martín et al., 2007; Kaltsoyannis and Plane, 2008; Gómez Martín and Plane, 2009). A distinct feature of iodine chemistry, with respect to the other halogens, is the formation of I\(_x\)O\(_y\) (where usually x = 2 and y = 2, 3, or 4) from recombination reactions of IO with itself (y = 2) and with OIO (y = 3), or OIO with itself (y = 4). Unambiguous discriminated observation of I\(_2\)O\(_3\) has been achieved only recently by means of photionization time-of-flight mass spectrometry (Gómez Martín et al., 2013a). This recent work also confirmed the minor role played by ozone in the formation of iodine aerosol (Saunders and Plane, 2005). Some other iodine oxides with different I/O stoichiometry (x ≠ 2) have been suggested to participate in complex mechanisms of particle formation (Gálvez et al., 2013; Gómez Martín et al., 2013a), albeit considerable uncertainty still exists about the chemistry and spectroscopy of these higher iodine oxides.

Table 2 presents the photochemical iodine reactions included in CAM-Chem. Absorption cross-sections and quantum yields for all species besides the I\(_2\)O\(_3\) have been taken from IUPAC-2008 (Atkinson et al., 2007, 2008) and JPL-2010 (Sander et al., 2011). \(\ast\) Radical organic products are not considered.

\(\ast\) Only the reaction channel reported in JPL 06-02 (Sander et al., 2006) is considered.

\(\ast\) Photolysis reactions only considered in the I\(_2\)O\(_3\) scheme. The absorption cross-sections reported in Sect. 2.2 (see Fig. 1) have been used.

Table 3. Iodine chemistry scheme in CAM-Chem: heterogeneous reactions.

<table>
<thead>
<tr>
<th>Sea-salt aerosol reactions</th>
<th>Reactive uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>IONO(_2) (\rightarrow) 0.5 IBr + 0.5 ICl</td>
<td>(\gamma = 0.01)</td>
</tr>
<tr>
<td>IONO(_2) (\rightarrow) 0.5 IBr + 0.5 ICl</td>
<td>(\gamma = 0.02)</td>
</tr>
<tr>
<td>HOI (\rightarrow) 0.5 IBr + 0.5 ICl</td>
<td>(\gamma = 0.06)</td>
</tr>
<tr>
<td>I(_2)O(_2) (\rightarrow)</td>
<td></td>
</tr>
<tr>
<td>I(_2)O(_3) (\rightarrow)</td>
<td></td>
</tr>
<tr>
<td>I(_2)O(_4) (\rightarrow)</td>
<td></td>
</tr>
</tbody>
</table>

Values based on the THAMO model (Saiz-Lopez et al., 2008) and implemented in CAM-Chem following Ordóñez et al. (2012). \(\ast\) Deposition of I\(_2\)O\(_3\) species on sea-salt aerosols has been included following the free regime approximation.
INO₂ and IONO₂ are also included in the chemical mechanism (Table 3) following the free regime approximation (McFiggans et al., 2000). Here we consider that the rate-limiting step of the recycling process is the uptake of the gaseous iodine species on the surface of a halogen-enriched (bromide and chloride) aerosol. Note that these recycling reactions constitute a net source of bromine and chlorine to the atmosphere, but represent only a change in partitioning for the case of iodine species. The non-reactive uptake of the atmosphere, but represent only a change in partitioning for the case of iodine species. The non-reactive uptake of the atmosphere, but represent only a change in partitioning for the case of iodine species.

Table 4 presents the Henry Law coefficients ($k_0$) and dry deposition velocities used to compute the removal of inorganic iodine from the gaseous phase via washout, scavenging in water and ice clouds, and dry deposition (Neu and Prather, 2012; Ordóñez et al., 2012). The vertical variation of the surface area density (SA) of sea-salt aerosols (SA_{SSALT}) and liquid droplets (SA_{LIQ}) used to compute the heterogeneous recycling reactions and the wet removal of inorganic iodine, respectively, is described and shown in Fig. 10a of Fernandez et al. (2014).

<table>
<thead>
<tr>
<th>Species</th>
<th>$k_0$ (M atm$^{-1}$)</th>
<th>Deposition velocity* (cm s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBr ice</td>
<td>$2.4 \times 10^4$</td>
<td>--</td>
<td>1</td>
</tr>
<tr>
<td>ICl ice</td>
<td>$1.1 \times 10^2$</td>
<td>--</td>
<td>1</td>
</tr>
<tr>
<td>HI</td>
<td>$7.8 \times 10^{-1}$</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>HOI - (J_{1O3}/Base)</td>
<td>$1.9 \times 10^3 / 4.5 \times 10^3$</td>
<td>0.75</td>
<td>1</td>
</tr>
<tr>
<td>IONO² ice</td>
<td>$1.0 \times 10^6$</td>
<td>0.75</td>
<td>2</td>
</tr>
<tr>
<td>IONO² ice</td>
<td>$3.0 \times 10^{-1}$</td>
<td>0.75</td>
<td>2</td>
</tr>
<tr>
<td>IO</td>
<td>$4.5 \times 10^2$</td>
<td>--</td>
<td>2</td>
</tr>
<tr>
<td>OIO</td>
<td>$1.0 \times 10^4$</td>
<td>--</td>
<td>2</td>
</tr>
<tr>
<td>I₂O₂</td>
<td>$1.0 \times 10^4$</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>I₂O₃</td>
<td>$1.0 \times 10^4$</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>I₂O₄</td>
<td>$1.0 \times 10^4$</td>
<td>1.0</td>
<td>2</td>
</tr>
</tbody>
</table>

* Dry deposition velocities are based on the THAMO model (Saiz-Lopez et al., 2008).
1 Values reported in Sander (1999).
2 Values based on the THAMO model (Saiz-Lopez et al., 2008).
3 Considering a dissociation constant $K_a = 3.2 \times 10^9$ and a temperature dependent coefficient $e = 9800$ K
4 Within the range of values given in the corresponding reference.
5 Virtually infinite solubility is represented by using a very large arbitrary number.
6 Value assumed to be equal to those of BrNO$_2$.
7 Species for which ice-uptake is considered following Neu and Prather (2012).

2.2 Absorption cross-sections of I$_2$O$_4$

Prominent featureless absorption bands of I$_2$O$_4$ species have been experimentally observed in the UV region (Bloss et al., 2001; Gómez Martín et al., 2005; Spietz et al., 2005). The photolysis thresholds of the iodine oxides are mostly in the near-infrared region (Gálvez et al., 2013). Therefore, it is plausible that in the atmosphere photochemical decomposition of I$_2$O$_4$ back to IO$_x$ will compete with thermal decomposition and uptake by aerosol, reducing the atmospheric losses by washout and/or scavenging. Based on the kinetic behaviour of the absorption spectra observed in the laboratory, tentative spectral assignments and estimation of the corresponding absorption cross-section have been reported. While Bloss et al. (2001) assigned the broadband absorption appearing under the IO spectrum to a single species (I$_2$O$_2$), Gómez Martín et al. (2005, 2007) obtained evidence of the two specie the spectra extracted and scaled to absolute absorption cross-section by Gómez Martín et al. (2005) (Fig. 1). Extraction of the I$_2$O$_4$ absorption spectrum from the observed I$_2$O$_5$ broadband absorption was unfeasible, and therefore, in the present work, a solution spectrum measured at the University of Leeds has been used. The I$_2$O$_4$ spectrum was measured at 1 nm resolution using a Perkin-Elmer Lambda 900 UV-Vis spectrometer in a 1 cm quartz cuvette (R. Sanders, personal communication, 2012). I$_2$O$_4$ was synthesized from commercial I$_2$O$_5$ / I$_2$ and H$_2$SO$_4$ (Sigma Aldrich). This made iodosulfate, which then, washed, converted to I$_2$O$_4$ (Daehlie and Kjekshus, 1964). Note that the gas phase absorption spectrum of I$_2$O$_4$ is likely to be blue-shifted with respect to its spectrum in solution and therefore this may result in overestimation of the atmospheric photolysis rates.

2.3 Model simulations

Total inorganic iodine (I$_x$) has been defined as

$$I_x = I + IO + HOI + IONO_2 + I_2O_4 + I_{minor} + I_{dihal},$$

(1)
The upper and lower limits of total inorganic iodine loading in the troposphere have been estimated by conducting simulations where the photolysis of I$_2$O$_y$ was allowed ($J_{I_2O_y}$) or neglected (Base), respectively. The last of a 3-year simulation was used to compute the iodine atmospheric burden for both cases. As the model is configured with prescribed sea surface temperatures and ice coverage for the 2000 decade (Rayner, 2003), results are not representative of the meteorology of any specific year, and annual averages are presented unless specifically mentioned. Three different vertical regions on consecutive non-overlapping altitude intervals were defined within the tropics (20° N–20° S) and mid-latitudes (50–20° N and 20–50° S): MBL, expanding from the ocean surface up to ∼900 m a.s.l (∼900 hPa); the FT, from ∼900 m (900 hPa) to ∼8.5 km (350 hPa); and the UT from ∼8.5 km (350 hPa) up to the model tropopause. 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 time (LT), respectively, for all latitudes and longitudes. Additionally, the Western Pacific (WP) warm pool area was defined by the equator (0°) and the 20° N parallels, and the 120 and 165° E meridians (see black rectangle in Fig. 7). Gas phase mole fractions for all species are given in ppbv or pptv, which are equivalent to the IUPAC recommended units nmol mol$^{-1}$ and pmol mol$^{-1}$, respectively (Schwartz and Warneck, 1995).

### 3 Results and discussions

The upper and lower limits of total inorganic iodine loading in the troposphere have been estimated by conducting simulations where the photolysis of I$_2$O$_y$ was allowed ($J_{I_2O_y}$) or neglected (Base), respectively. The last of a 3-year simulation was used to compute the iodine atmospheric burden for both cases. As the model is configured with prescribed sea surface temperatures and ice coverage for the 2000 decade (Rayner, 2003), results are not representative of the meteorology of any specific year, and annual averages are presented unless specifically mentioned. Three different vertical regions on consecutive non-overlapping altitude intervals were defined within the tropics (20° N–20° S) and mid-latitudes (50–20° N and 20–50° S): MBL, expanding from the ocean surface up to ∼900 m a.s.l (∼900 hPa); the FT, from ∼900 m (900 hPa) to ∼8.5 km (350 hPa); and the UT from ∼8.5 km (350 hPa) up to the model tropopause. 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 time (LT), respectively, for all latitudes and longitudes. Additionally, the Western Pacific (WP) warm pool area was defined by the equator (0°) and the 20° N parallels, and the 120 and 165° E meridians (see black rectangle in Fig. 7). Gas phase mole fractions for all species are given in ppbv or pptv, which are equivalent to the IUPAC recommended units nmol mol$^{-1}$ and pmol mol$^{-1}$, respectively (Schwartz and Warneck, 1995).

### 3.1 The partitioning of VSL iodine source gases

Figure 2 shows the vertical profiles of the four major VSL iodocarbons together with their photochemical decomposition rates within the tropics. On an annual average, the total organic iodine abundance results in ∼0.8 pptv in the MBL and ∼0.1 pptv in the FT (Fig. 2a). The percentage contribution of each individual VSL species to total organic iodine is approximately 82 % (96 %), 12 % (2.7 %), 5 % (0.8) and 1 % (0.1 %) for CH$_3$I, CH$_2$ICl, CH$_3$IBr and CH$_3$Br in the MBL and (FT), respectively. Iodine-containing di-halocarbons are photolysed almost entirely within the MBL, and the predominant organic species in the free troposphere is methyl iodide. As a consequence, CH$_3$I is the only iodocarbon reaching the lower tropical tropopause layer (TTL) by efficient convection; although integrated in the tropics it represents a negligible (∼10$^{-3}$ pptv) carbon-bonded residual at the coldest point tropopause ($t_{pt}$ ≈ 380 K, approx. at 17 km) in agreement with previous studies that determined an inconsiderable
injection of VSL iodocarbons into the stratosphere (Montzka et al., 2011; Tegtmeier et al., 2013).

Even when the added photodecomposition of CH$_2$I$_2$, CH$_2$Br and CH$_3$Cl within the MBL represents an additional source of inorganic iodine comparable to that of CH$_3$I (Fig. 2b), several studies have suggested that an additional source of active iodine must exist at the sea surface in order to reconcile open ocean measurements of IO with current knowledge of iodine and chemistry (Jones et al., 2010; Mahajan et al., 2010; Gómez Martin et al., 2013b; Großmann et al., 2013). Within CAM-Chem, the inorganic iodine (HOI / I$_2$) released from the tropical oceans following the work of Carpenter et al. (2013) and MacDonald et al. (2014) (see red dot in Fig. 2b, $\sim$6.3 $\times$ 10$^3$ atoms cm$^{-3}$ s$^{-1}$) is an order of magnitude higher than that from all organo-iodine species combined (5.7 $\times$ 10$^3$ atoms cm$^{-3}$ s$^{-1}$ at the surface level and totalling $\sim$1.0 $\times$ 10$^3$ atoms cm$^{-3}$ s$^{-1}$ in the MBL), and is the dominant source of iodine within the MBL. Another important source of reactive iodine in the lower troposphere is the photolysis of the diatomic ICl and IBr species recycled by heterogeneous reactions over sea-salt aerosols (red line in Fig. 2b), which we calculate to be the most important process releasing atomic iodine when integrating the first 5 km in the marine atmosphere. Note that the implementation of sea-salt recycling in CAM-Chem for iodine species does not constitute a net source of iodine to the troposphere (see Table 3) but represents only a change in iodine partitioning that slows down the conversion of reactive iodine into reservoir species with greater washout efficiencies (i.e. HOI or IONO$_2$). The photolysis of CH$_3$I represents 10, 60 and 83% of the total iodine sources from VSL photodecomposition within the MBL, FT and UT respectively, whereas in the lower TTL the source of iodine becomes almost solely CH$_3$I. The other VSL iodocarbon with a non-negligible contribution to I$_x$ in the FT and UT is CH$_2$ICI – its I atom release can reach 22% (FT), 10% (UT) and 5% (TTL) of the total iodine source. Note that from all the VSL species represented in the model CH$_2$ICI is the di-halogen iodocarbon with the longest lifetime ($\sim$8 h) and it represents the strongest oceanic VSL source on an iodine atom basis.

The very rapid photolysis of iodocarbons, compared to transport times, makes the relative contribution from each VSL species to the inorganic iodine release to be almost independent of the spatial scale considered. For example, on an annual average, from the total tropical release of atomic iodine at 12 km 90% arise from CH$_3$I and 7% from CH$_2$ICI, while their respective percentage contributions are 85 and 10% within the convective WP warm pool during February. This is in contrast to the longer-lived VSL bromocarbons, where the total amount of atomic bromine released from each independent species at a given altitude, within the TTL, strongly depends on the strength of convection (Fernandez et al., 2014). For VSL iodocarbons, the I$_x$ loading in the FT and UT depends mainly on the geographical distribution and intensity of CH$_3$I oceanic emissions, which presents localized areas with stronger fluxes, such as the Indian Ocean and the WP region. Ordóñez et al. (2012) also found that using an emission cycle with non-zero emissions during the night, the monthly average concentrations of CH$_2$IX species increase – e.g. the iodocarbons, which are the VSL species with shortest lifetimes, can temporally accumulate in the MBL at night and be transported to higher altitudes. This highlights the importance of experimentally determining the shape of the diurnal emission profile to estimate the overall impact of VSL iodocarbons at different heights.

### 3.2 Iodine burden in the troposphere and the role of I$_x$O$_y$

The fast reactions IO + IO, IO + OIO and OIO + OIO lead to the formation of significant levels of I$_2$O$_2$, I$_2$O$_3$ and I$_2$O$_4$, respectively. As within the Base scheme only thermal decomposition and deposition onto background aerosol of iodine oxides are allowed, the levels of I$_x$O$_y$ build up in the atmosphere, and become the most abundant species in the FT and UT (Fig. 2c). If I$_x$O$_y$ were not photolabile, they would represent 30% of the total I$_x$ abundance in the MBL and more than 70% in the FT and UT. This large mass of iodine in the atmosphere is currently unaccounted for and subject to a large degree of uncertainty about the photochemistry of higher iodine oxides. This presents a fundamental problem in the quantification of iodine chemistry and its effect in the atmosphere, as the particle nucleating I$_x$O$_y$ species do not release active iodine back to the gaseous phase (especially in the FT and UT where temperatures are too low for thermal decomposition to be efficient), representing an effective sink of atmospheric iodine. As many uncertainties still exist on which are the dominant photochemical processes affecting I$_x$O$_y$ species, hereafter, we present our best estimate of the upper and lower range of tropospheric iodine loading and its partitioning for the Base and I$_x$O$_y$ schemes defined in Sect. 2.3. Most likely, an intermediate mechanism between these two scenarios controls the iodine recycling in the real atmosphere, with a portion of the I$_x$O$_y$ being removed by wet/dry deposition, another one forming larger iodine aggregates which will likely be lost to aerosol, and the rest being recycled to IO$_x$ in the gas phase by photolysis.

Figure 3a shows the range of vertical distribution of the main annually averaged daytime iodine species within the tropics (20$^\circ$N–20$^\circ$S) for the Base and I$_x$O$_y$ schemes. From the surface to about 7–8 km HOI is the main daytime iodine reservoir. Above that height, atomic iodine becomes the dominant iodine species during the day from the mid-to upper troposphere, resulting in an averaged 19% (58%) of the total daytime I$_x$ in the UT for the Base and (I$_x$O$_y$) schemes, respectively. On an annual average, surface daytime IO mixing ratios over the tropical oceans range from 0.45 to 0.7 pptv in agreement with recent ship-borne measurements performed over remote open oceans (Mahajan et
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Figure 3. Lower and upper limits of I$_y$ abundances within the tropical troposphere (20° N–20° S): (a) main inorganic species at noon (11:30–12:30 LT); (b) major I$_y$ species at midnight (23:30–00:30 LT). The lower limit corresponds to the Base scheme, while the upper limit is for the J$_{IxOy}$ scheme.

al., 2012; Großmann et al., 2013). Above the MBL, IO vertical profiles remain in the range (0.1–0.25) pptv between 2 and 8 km, in agreement with recent measurements in the FT performed over the tropical Atlantic (Puentedura et al., 2012) and Pacific (Dix et al., 2013) oceans. The tropospheric IO vertical profiles show two distinct vertical shapes depending on the inclusion or not of the I$_{xOy}$ photolysis: within the Base scheme there is an evident reduction of IO concentrations with altitude (IO$_{12km}$ = 0.04 pptv) due to the large conversion of IO$_x$ to un-reactive I$_xOy$ in the UT; while for the J$_{IxOy}$ scheme high levels of IO are maintained throughout the FT and up to the UT (IO$_{12km}$ = 0.16 pptv) (see Sect. 3.4).

Dix et al. (2013) reported IO vertical profiles over the Pacific Ocean and suggested the existence of an additional process (which they proposed to be heterogeneous sea-salt recycling) in order to sustain the elevated IO levels observed throughout the mid- and upper FT. Our modelling results indicate that heterogeneous recycling on sea-salt can contribute to the IO profile up to about 5 km (Fig. 2b), however it is very unlikely that reactions on sea-salt can be a source of iodine towards the upper FT, except within convective regions, due to its negligible number concentration at those heights. Instead, we suggest that the combined release of I atoms from CH$_3$I photolysis and the photolytic recycling of gaseous I$_xOy$ within the J$_{IxOy}$ scheme can account for the increase in IO$_x$ lifetime required to reconcile our current understanding of iodine chemistry to recent field measurements throughout the mid- to upper troposphere (Fig. 3a, see also Sect. 3.4).

The comparative release of reactive iodine species due to CH$_3$I photolysis (defined as d[I]/dt) and that arising from the thermal and photolytic breakdown of I$_xOy$ (defined as d[I$_{xOy}$/dt = -d[I$_{xOy}$/dt]) is shown in Fig. 4. Note that the losses of higher oxides are equivalent to the production of reactive iodine and do not represent a net sink of iodine in the atmosphere, but a change in partitioning between different I$_y$ species. Photochemical decomposition of CH$_3$I accounts for up to 501 atoms cm$^{-3}$ s$^{-1}$, within the MBL, and between 2 and 8 atoms cm$^{-3}$ s$^{-1}$ in the tropical FT (Fig. 4a). As Base and J$_{IxOy}$ schemes consider identical VSL sources, the latitudinal distributions are equivalent for both schemes. Within the Base scheme the release of inorganic iodine from VSL sources in the FT is up to three orders of magnitude larger than the contribution from I$_xOy$ thermal decomposition (Fig. 4b), and controls the tropospheric inorganic iodine burden. Due to the slow thermal breakdown of higher oxides, I$_xOy$ accumulate in the FT (Fig. 2c, see also Sect. 3.4). When the photolysis of I$_xOy$ is allowed, this pro-

Figure 4. Annual distribution of reactive iodine (IO$_x$ = I + IO) sources as a function of latitude and altitude: (a) atomic iodine release from photolysis of CH$_3$I; (b) IO$_x$ production from thermal decomposition of I$_xOy$ for the Base scheme; (c) photodecomposition of higher oxides within the J$_{IxOy}$ scheme. Note that for (b) and (c), the photolysis of OIO to I + O$_2$ (Gómez Martín and Plane, 2009) is so efficient that the formation of OIO from I$_xOy$ (Table 1) is computed here as IO$_x$. 24 h averages are shown in all cases.
cess constitutes the most important source of reactive iodine in the tropical free troposphere, recycling back more than 500 IO molecules cm\(^{-3}\) s\(^{-1}\), and avoiding a large I\(_x\)O\(_y\) accumulation. As a consequence, larger amounts of I\(_2\)O are maintained at higher altitudes (Fig. 3a). It is worth noting that the photodecomposition of CH\(_3\)I is the first step providing iodine atoms in the FT, and without the contribution from this organic precursor the inorganic iodine loading in the FT and UT would be significantly reduced. Additionally, direct transportation of I\(_x\) species from the MBL, sustained by stochiometric heterogeneous recycling on sea-salt aerosol, increase the impact of iodine chemistry on the ozone budget as described in Sect. 3.5.

It is worth noting how the crossing-point height for the I–IO (\(~7\) km), I–HOI (\(~9\) km) and IO–HOI (\(~11\) km) vertical noontime profiles occurs at the same altitude, regardless of the consideration or not of the photolysis of the I\(_2\)O (see Fig. 3a). This confirms that the steady state reached is nearly independent of the total amount of I\(_x\) as expected due to the rapid photochemical time constants of the gaseous iodine system. The importance of constraining the absolute I\(_x\) loading in the mid- and upper troposphere is more evident if we consider that the relative oxidative potential of iodine chemistry is greater in the upper troposphere, and that \(~80\%\) of the halogen-mediated tropospheric ozone loss occurs above 800 hPa (Saiz-Lopez et al., 2012b, see Sect. 3.5).

During the night, the main reservoir species in the mid- and upper troposphere is HOI (Fig. 3b), which accounts for 70\% of the total nighttime I\(_x\) in the FT for the J\(_1\)O\(_2\) scheme. Therefore, HOI is the most abundant iodine species in the lower troposphere both during the day and at night, and its washout efficiency controls the total atmospheric iodine burden. Indeed, the Henry law constant for HOI (K\(_H\)OI) has been adjusted between a more (Base) and less (J\(_1\)O\(_2\)) efficient value within the range of measurements and uncertainties reported in the literature (Sander, 1999; see also Table 4). This results in a total washout rate within the tropics in the range of \(~6–7 \times 10^7\) atoms (I) cm\(^{-2}\) s\(^{-1}\). For the J\(_1\)O\(_2\) scheme, \(~95\%\) of the wet-removal occurs in the MBL and FT and is controlled by the uptake on liquid droplets of HOI, IONO\(_2\) and I\(_x\)O\(_y\) (42\%, 21\% and 16\% respectively). The Base scheme presents a comparatively larger contribution from I\(_x\)O\(_y\) scavenging (30\% compared to 12\% for IONO\(_2\)) due to the higher oxide accumulation. Note that from the overall I\(_x\)O\(_y\) sinks, only \(~15\%\) occurs due to irreversible deposition on sea-salt aerosols.

Within the J\(_1\)O\(_2\) scheme, the IONO\(_2\) abundance increases significantly above 10 km, representing the most abundant nighttime inorganic reservoir in the TTL (IONO\(_2\) \(~3\) km = 0.4 pptv) and the main sink of iodine at these heights. In the case of the Base scheme, since less I\(_2\) is available (i.e. due to the irreversible conversion of IO to I\(_2\)O\(_2\) in the cold UT) for reaction with NO\(_2\), the IONO\(_2\) levels in the UT are considerably lower (Fig. 3b), and most of the iodine remains in the form of I\(_x\)O\(_y\). This implies that once I\(_x\)O\(_y\) are formed within the Base scheme, they do not further release active iodine back to the gas phase, and then behave as an unreactive sink of iodine that accumulates in the gas phase. As during daytime, the nocturnal crossing altitude of the HOI and IONO\(_2\) vertical profiles is equivalent for both schemes (\(~15\) km), indicating that the relative partitioning of the main I\(_x\) species does not depend on the overall I\(_x\)O\(_y\) or total I\(_x\) abundances.

### 3.3 The tropical ring of atomic iodine

Levels of daytime atomic I increase significantly in the middle and upper troposphere due to the low ozone concentrations and temperatures prevailing in these regions, which slow down the formation of IO by the I + O\(_3\) Arrhenius type reaction (Sander et al., 2011). Under these conditions, we simulate a daytime "tropical ring of atomic iodine" with a latitudinal extent from 30°N to 30°S (Fig. 5). Within this inhomogeneous tropical ring, annual zonal average atomic I peaks at 0.2 and 0.65 pptv for the Base and J\(_1\)O\(_2\) schemes, respectively, accounting for up to 70\% of the total annually averaged I\(_x\) in the tropics (black contour lines in Fig. 5).

The altitude at which the maximum modelled I atom levels are observed depends on the photochemical scheme considered: for the Base scheme the atomic ring extends from 7 to 15 km, peaking at \(~11\) km (Fig. 5a–c, top panels), while for the J\(_1\)O\(_2\) scheme it expands from 8 to 17 km, with maximum abundances located at \(~14\) km (Fig. 5d–f, bottom). The longitudinal (Fig. 5b, e) and temporal (Fig. 5c, f) variation of the atomic iodine tropical ring suggests that atomic I is globally and annually the most abundant daytime iodine species within the tropics from about 9 km up to the tropopause. The highest I atom concentrations within the tropical ring are modelled to exist within regions of strong oceanic sources and during periods of strong convection, when large amounts of inorganic iodine are rapidly transported from the MBL to the FT and UT. For example, within the WP region, the monthly I atom abundance peaks at 0.30 and 0.90 pptv for the Base and J\(_1\)O\(_2\) schemes, respectively.

In both simulated schemes the atomic tropical ring and the relative I/I\(_x\) distributions are coincident in altitude. Note however that the ultimate fate of the higher iodine oxides in the atmosphere is very uncertain, and within the Base scheme there is an increasing accumulation of I\(_x\)O\(_y\) with altitude. As a consequence, the percentage contribution of atomic iodine to I\(_x\) for the Base scheme is at least halved with respect to the J\(_1\)O\(_2\) scheme. If I\(_x\)O\(_y\) species are not considered for the Base scheme, then the I/I\(_x\) contour lines for both simulations present equivalent values (see Sect. 3.4).

The tropical ring of atomic iodine is a photochemical phenomenon defined by the low abundance of ozone and cold conditions of the upper troposphere. While the absolute ambient levels of iodine species depend on the total inorganic loading of the tropical troposphere (i.e. washout rates, ice-uptake), the unusual feature of the halogen atom being
Figure 5. The “tropical ring of atomic iodine” for the Base (top) and $J_{I,O_3}$ (bottom) schemes: (a, d) annual zonal average; (b, e) annual meridional average abundance of atomic I within the tropics ($20^\circ$N–$20^\circ$S); and (c, f) seasonal evolution of the zonally averaged atomic I ring within the tropics. The colour scale represents noontime volume mixing ratios (pptv) while black contour lines show the percentage contribution of atomic I to $I_y$.

the predominant species is an implicit consequence of the fast thermal/photochemical interplay within the main iodine chemistry cycling scheme (see Tables 1 and 2) and the natural state of the tropical upper troposphere (i.e. high photolysis rates, lower $O_3$ than in the stratosphere and low temperatures). As the I atom ring is photochemically driven, it is present only in the illuminated portion of the Earth and it circles the tropics with the sun. Fernandez et al. (2014) have suggested a co-existent “tropical ring of atomic bromine” within the TTL. The driving mechanisms of these atomic halogen rings are identical. The distinct features between their relative peak altitude or abundances are due to the different photodissociation rates for $J_{IO}$ and $J_{BrO}$, and the different lifetimes of the organic VSL halocarbons that constitute the main source of reactive iodine (CH$_3$I) and bromine (mostly CHBr$_3$) in the upper tropical troposphere.

### 3.3.1 The I / IO ratio in the troposphere

As described above, atomic iodine levels surpass IO abundances above $\sim\text{5–6 km}$, therefore a ratio I / IO > 1 must exist in the middle and upper troposphere. Figure 6a shows the vertical variation of the I / IO ratio for the Base and $J_{I,O_3}$ schemes, averaged over different regions and periods within the tropics. A ratio of I / IO > 1 is calculated from the mid-troposphere through the tropical cold point tropopause. Notwithstanding the photochemical treatment of the higher iodine oxides, both schemes present identical I / IO vertical profiles with maximum values occurring at coincident altitudes ($\sim\text{14–15 km or } \sim\text{130 hPa}$), which indicate that the occurrence of I / IO > 1 is independent of $I_y$. The peak magnitude strongly depends on the local $O_3$ abundance and the cold temperatures prevailing in the upper troposphere (Fig. 6b). The ratio maximizes during periods and within regions of strong convection, when poor-ozone air-masses are rapidly transported from the lower troposphere to the lower TTL.
Then, both Base and J\textsubscript{I\textsubscript{x}O\textsubscript{y}} schemes show a ratio enhancement from I/IO ≈ 3 for the tropical annual average to ∼8 within the Western Pacific (WP) warm pool during February. Within the WP region and during a vigorous convective event transporting large amounts of inorganic iodine directly into the lower TTL, the model I/IO ratio reached values as high as ∼20 for both schemes (Fig. 6a). This highlights the importance of measuring atomic iodine levels in the upper troposphere in order to constrain our current knowledge of the iodine burden in this region of the atmosphere.

The O\textsubscript{3} concentration and the ambient temperature are the dominant factors in determining the ratio. The ozone levels and surrounding temperatures determining the I/IO > 1 range from 25 to 200 ppbv and from 250 to 190 K at the lower and higher boundary limit, respectively (Fig. 6b). Following a steady-state approximation considering the two most important reactions involving I and IO species, the ratio can be calculated using the IO photolysis and the I reaction with O\textsubscript{3}:

\[
\frac{[I]}{[IO]} = \frac{J_{\text{IO}}}{k_{1}\text{O}_3[O_3]}.
\] (5)

The contribution from other species that react with atomic I is negligible (see Table 1). Note that even when both schemes result in a similar ratio vertical profile, the J\textsubscript{I\textsubscript{x}O\textsubscript{y}} scheme calculates slightly smaller ratios because the assumed photochemical breakdown of I\textsubscript{x}O\textsubscript{y} releases IO radicals back to the gas phase, reducing the I/IO ratio.

The geographical distributions of the tropical ring of atomic iodine and the I/IO ratio at an altitude of 14 km are shown in Fig. 7. Results for the J\textsubscript{I\textsubscript{x}O\textsubscript{y}} scheme are presented since the maximum values of both the iodine ring and the ratio are coincident in altitude when the photolysis of I\textsubscript{x}O\textsubscript{y} are considered. Both distributions clearly maximize in the Western Pacific region and the Indian Ocean, highlighting the importance of convective transport and strength of oceanic sources in the occurrence of this natural phenomenon. The I/IO ratio follows the geographical distribution of O\textsubscript{3} and temperature, both of which locally minimize in the same region where the ratio peaks (Fig. 7c, d). Note also that I/IO > 1 only occurs within the tropical latitudes, decreasing to values smaller than unity polewards of 30° N/30° S. Hence, we suggest that experimental programs oriented to reduce the uncertainties of iodine chemistry in the tropical troposphere should also include a strategy for the direct measurements of daytime atomic iodine besides the usually targeted IO radical.

### 3.4 The partitioning of inorganic iodine

Figure 8 shows the 24 h annual zonal average distribution of the main iodine species (besides atomic iodine) for the Base (left panels) and J\textsubscript{I\textsubscript{x}O\textsubscript{y}} (right panels) schemes. With the exception of IONO\textsubscript{2}, which is the only species with a strong hemispheric gradient in the MBL due to the larger anthropogenic NO\textsubscript{x} levels prevailing over the northern oceans, all inorganic iodine species abundances maximize within the tropical regions. IO abundance in the FT is reduced to ∼1/3 of its concentration in the MBL, maintaining an approximately constant abundance with height between 2 and 8 km. In the Base scheme, noon IO levels in the tropics ≥ 0.1 pptv between 2 and 7–8 km result from halogen recycling on sea-salt (active up to about 4–5 km) and photolysis of CH\textsubscript{3}I. Above 7–8 km, and up to the tropopause, noon IO levels ≥ 0.1 pptv can only be sustained by the combined release of iodine atoms from the photodissociation of CH\textsubscript{3}I, whose concentration is ∼0.1 pptv from 4 to 12 km, and the photolysis of I\textsubscript{x}O\textsubscript{y} that increases the lifetime of IO\textsubscript{x} in the gas phase (see Fig. 4).
Figure 8. Annual zonal average distribution of the main I\textsubscript{y} species in the troposphere for the Base (left) and \textit{J\textsubscript{I, O\textsubscript{3}}} (right) schemes. The colour scale represents 24-h average volume mixing ratios (pptv) while black contour lines show the percentage contribution of each species to I\textsubscript{y}.
Figure 8 shows that HOI is the dominant iodine species, representing more than 60% of total I$_y$ between 1 and 8 km for the $J_{Iy}$ scheme (HOI is the dominant species both during the day and at night, see Figs. 3 and 11). HI and IONO$_2$ contributions represent less than 5% of total I$_y$ while IONO$_2$ exceeds 10% in the lower troposphere of the Northern Hemisphere. Note how the abundance of I$_yO_3$ increases significantly with altitude for the case of the Base scheme, due to decreasing temperatures that prevent their thermal decomposition (Fig. 8i). This shows that for the Base scheme there is a permanent conversion of the major active iodine species to I$_yO_3$, which turns out to be a non-reactive reservoir that does not recycle back to active IO$_x$ (see grey shading in Fig. 9a). Up to 70% of the total I$_y$ is modelled to be transformed to unreactive I$_yO_3$ in the upper troposphere within the Base scheme, representing a fundamental problem to our current knowledge of iodine chemistry. Even when the tropospheric washout efficiency of I$_yO_3$ is assumed to be larger than that of HOI ($k_{Iy}^{HOI} > k_{Iy}^{IyO_3}$, see Table 4), the higher oxides’ production is so large, and their thermal decomposition so slow, that their final fate within the Base scheme is to accumulate in the atmosphere. Then, the modelling experiment performed here indicates that either: (i) an unrecognized removal process for I$_yO_3$ must exist in the FT and UT, (ii) a substantial accumulation of unreactive I$_yO_3$ prevails in the upper troposphere or (iii) a decomposition pathway releasing active iodine, such as the photodecomposition proposed in the $J_{IyO_3}$ scheme, occurs. As to the authors’ knowledge there is no evidence for (i) or (ii), we suggest, based on experimental and theoretical studies (i.e. Gómez Martín et al., 2005; Saiz-Lopez et al., 2008) that the photochemistry of I$_yO_3$ should be further investigated in order to reduce uncertainties on the important chemical impacts of iodine chemistry. With the assumptions made in the $J_{IyO_3}$ scheme, the I$_yO_3$ levels are clearly reduced in favour of other inorganic iodine species (see Fig. 9b), which strongly affect their potential impact on tropospheric ozone destruction (see Sect. 3.5).

Figure 9 shows the vertical variation of the contribution of organic and inorganic species to the total iodine burden within the tropical atmosphere. The only precursor species with a photochemical lifetime long enough to reach the UT is CH$_3$I, whose abundance remain at ~0.1 pptv until the lower TTL (~12 km) is reached. There is a small contribution of minor VSL iodocarbons (CH$_2$I$_2$, CH$_2$IBr and CH$_2$ICl), but most of them are decomposed within the MBL. Note that below 5 km, there is also a non-negligible contribution of dihalogen molecules (ICl+IBr+I$_2$), which on average for the whole year, represent up to 0.25–0.30 pptv of I$_y$ integrated within the tropical MBL. At the ocean surface, the modelled overall abundance of I$_2$, ICl and IBr species at nighttime reaches 1.3 (1.7) pptv for the Base (J$_{IyO_3}$) schemes, respectively (Fig. 3b). The predominant contribution of these diatomic species to nighttime I$_y$ decreases rapidly with altitude due to the rapid reduction in the availability of sea-salt aerosol surface, upon which IBr and ICl are formed following the uptake and heterogeneous recycling of IONO$_2$, INO$_2$ and HOI (see Table 3). Additionally, an abiogenic source of I$_2$ (as well as HOI) is introduced in the model at the ocean surface following the oxidative reaction of ozone with aqueous iodide (see Sect. 2.1).

Within the tropics, approximately half of this inorganic oceanic flux is released during the night, resulting in the direct buildup of I$_2$ in the lower atmosphere, as well as an indirect buildup of ICl and IBr due to the heterogeneous recycling of HOI on sea-salt aerosols. Up to 50% of the nighttime I$_y$ within the MBL is in the form of I$_2$ + IBr + ICl. The relative contribution of I$_2$, IBr and ICl to the overall di-halogen contributions within the MBL are, respectively, 68, 16 and 16% for the Base scheme, and 53, 23 and 23% for the $J_{IyO_3}$ scheme. Note that the contribution of...
Figure 10. Zonal additive distribution of main organic and inorganic iodine species at different altitudes for the Base (left) and $J_{1, \text{IO}_3}$ (right) schemes. 24 h average volume mixing ratios (pptv) are presented at approximate heights of 1, 3, 6, 9, 12 and 15 km. Minor organic and inorganic species have been lumped together for simplicity (see text for details).
Figure 11. Diurnal variation of main inorganic iodine species at different altitudes for the Base (left) and J_{xOy} (right) schemes. Tropical averages considering locations with equivalent local times have been computed. Results are shown at approximate heights of 1, 3, 6, 9, 12 and 15 km.
the minor iodine species ($I_{\text{minor}}$) represents less than 5% of $I_y$ in both schemes.

Compared to the organic portion, the inorganic fraction is the dominant component of the total iodine budget for both schemes, with $I_{y}$ representing more than 90% of total iodine through the mid- to upper troposphere (Fig. 9). This is in clear contrast to the bromine partitioning in the troposphere where, even if the abundant long-lived halons and CH$_3$Br are left aside and just VSL bromocarbons are considered, only 30–40% of bromine is inorganic in the FT, with the dominant component being the organic VSL portion (Fernandez et al., 2014).

Figure 10 shows the annual additive zonal distribution of iodine species. Results are presented at selected heights of around 1, 3, 6, 9, 12 and 15 km for the Base (left panels) and the $J_{1\text{O}_2}$ (right panels) schemes. The rapid conversion of organic VSL iodocarbons (mainly CH$_3$I) to inorganic iodine as the altitude increases (and across latitudes) as well as the above-mentioned accumulation of I$_2$O$_y$ in the Base scheme, are clearly appreciated in Fig. 10. Note that even when the total inorganic loading for the $J_{1\text{O}_2}$ scheme is only 10–20% larger than for the Base scheme, the absolute abundance of the main $I_y$ species (HOI, I and IO) can be up to a factor of $\sim$5 greater when I$_2$O$_y$ are photolysed. Indeed, if I$_2$O$_y$ are not considered when computing the total inorganic iodine (i.e. defining an equivalent magnitude $I_{E}^{y} = I_{y} - I_{2\text{O}_y}$), then the relative contributions $I/I_{E}^{y}$, IO/$I_{E}^{y}$ and HOI/$I_{E}^{y}$ for the Base scheme are equivalent to $I/I_y$, IO/$I_y$ and HOI/$I_y$ for the $J_{1\text{O}_2}$ scheme. This confirms the rapid establishment of the photochemical steady state for the gaseous iodine system and the inert role of I$_2$O$_y$ on altering the $I_y$ partitioning for the Base scheme, thereby indicating that I$_2$O$_y$ production could basically be treated as an efficient sink of inorganic iodine, unless their photodissociation is considered.

For the same heights as Fig. 10, the average diurnal variation of the main iodine species is illustrated in Fig. 11. In the tropics, I and IO follow a diurnal concentration profile with a characteristic top-hat shape due to the fast photochemical constants of the iodine system which allows the rapid occurrence of the I–IO steady state. Note that the diurnal top-hat shape of IO is also influenced by the daytime loss of IO by reaction with HO$_2$. IO is the dominant daytime species below 5 km, while atomic iodine dominates above that height, defining the diurnal temporal evolution of the tropical I ring. IO levels show a double peak at dawn and dusk, which is most evident at lower altitudes. This is attributed to the reduced photodissociation of the IO radical during sunrise and sunset, particularly at lower heights, which favours the displacement of the steady state towards IO. During daylight hours, both I and IO abundances remain almost constant with time, while at nighttime they are completely converted to the reservoir species HOI and IONO$_2$. The balance between the nighttime reservoirs species is shifted from the predominance of HOI in the low- to mid-troposphere to that of IONO$_2$ in the UT, following the increase in NO$_2$ concentrations towards the upper troposphere. Overall, the diurnal variation of inorganic iodine shown here for the tropical upper troposphere, with elevated levels of I and IO at daytime and conversion to HOI and IONO$_2$ at nighttime, is in line with previous photochemical calculations of iodine in the tropical UT (Butz et al., 2009). Note that in the Base scheme I$_2$O$_y$ shows a flat diurnal concentration profile whereas in the $J_{1\text{O}_2}$ scheme the I$_2$O$_y$ daytime concentrations are negligible, due to efficient photolysis, and are only above pptv levels at night although at much lower abundances than IONO$_2$ and HOI. In both schemes the HOI photolysis dominates the early morning release of I atoms, compared to IONO$_2$, as evidenced by the faster decrease of HOI throughout sunrise (Fig. 11); this difference becomes smaller with altitude. This is due to the absorption spectrum of HOI in the visible as opposed to the strong absorption cross-section of IONO$_2$ in the ultraviolet (below 300 nm) (Saiz-Lopez et al., 2012a). During the daytime, HOI is the main species up to about 6 km; at higher altitudes in the troposphere the accumulation of I$_2$O$_y$ in the Base scheme and the very rapid interplay between I and IO in the $J_{1\text{O}_2}$ scheme dominate daytime $I_y$.

3.5 Implications for tropospheric ozone

Figure 12 presents the annual tropospheric ozone difference between the Base and $J_{1\text{O}_2}$ schemes as a function of altitude and latitude. The O$_3$ changes increase from $\sim$0.5 ppbv in the tropical MBL to up to $\sim$2.5 ppbv in the UT of the mid-latitudes (Fig. 12b) following the increase of O$_3$ abundances as the latitude and altitude increase (Fig. 12a). The ozone differences show a pronounced hemispheric dependence, with greater percentage changes (with respect to the Base scheme) of $\sim$5–6% for the SH due to the reduced impact of anthropogenic O$_3$ precursors, as compared to the NH. The ($J_{1\text{O}_2}$ – Base) differences shown in Fig. 12b are of the same magnitude as those found between a pair of non-iodine simulations including (OnlyBr) and neglecting the bromine contributions from VSL bromocarbons (NoVSL). This suggests that the uncertainties on the impact of iodine chemistry on the ozone budget (i.e. uncertainties in the photochemistry of I$_2$O$_y$) are of the same magnitude as the overall impact of tropospheric bromine chemistry from VSLs (OnlyBr – NoVSL, Fig. 12d). Indeed, even when the lower atmospheric iodine loading is considered (Base – OnlyBr, Fig. 12c) the impact on tropospheric ozone at $\sim$5 km (400–500 hPa) is equivalent to that obtained when only bromine chemistry is considered. This all highlights the need for further experimental research on the photochemical characterization of I$_2$O$_y$.

Figure 13 presents the absolute (Fig. 13a) and relative (Fig. 13b) vertical range of ozone loss rate between the Base and $J_{1\text{O}_2}$ schemes for each chemical family that participates in tropospheric odd oxygen (O$_x$) loss cycles. The O$_x$ loss rates equations for the ozone-depleting families considered in this work are presented in Table 5. The formalism used here is based on the catalytic cycles and chemical fam-
Table 5. Odd oxygen (O$_3$) loss rates reactions grouped by family cycles.

<table>
<thead>
<tr>
<th>Family</th>
<th>Reaction</th>
<th>$\Delta$O$_3$</th>
<th>Odd oxygen loss$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_x$</td>
<td>O + O$_3$ → 2 × O$_2$</td>
<td>-2</td>
<td>O$<em>3$ Loss = 2 × R$</em>{O+O_3}$ + R$_{O1D+H_2O}$</td>
</tr>
<tr>
<td></td>
<td>O(1D) + H$_2$O → 2 × OH</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>HO$_x$</td>
<td>HO$_2$ + O → OH + O$_2$</td>
<td>-2$^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HO$_2$ + O$_3$ → OH + 2 × O$_2$</td>
<td>-2$^2$</td>
<td></td>
</tr>
<tr>
<td>NO$_x$</td>
<td>NO$_2$ + O → NO + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO$_3$ + h$^\nu$ → NO + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>BrO$_x$+ ClO$_x$</td>
<td>ClO + O → Cl + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl$_2$O$_2$ + h$^\nu$ → 2 × Cl + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ClO + HO$_2$ → HOCIO + O$_2$</td>
<td>-2$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BrO + O → Br + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BrO + HO$_2$ → HOBr + O$_2$</td>
<td>-2$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BrO + ClO → Br + Cl + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BrO + ClO → BrCl + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>IO$_x$</td>
<td>IO + O → I + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>OIO + h$^\nu$ → I + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IO + HO$_2$ → HOI + O$_2$</td>
<td>-2$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IO + BrO → I + Br + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IO + ClO → I + Cl + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IO + ClO → ICl + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ $R_{A+B}$ is the reaction rate for reaction A+B=products and $J_C$ is the photodissociation rate constant (i.e. photolysis × concentration) for C+h$^\nu$→products. Units are molec.cm$^{-3}$s$^{-1}$.

$^2$ HO$_x$ loss cycles represent a net change 2O$_3$ → 3O$_2$ ($\Delta$O$_3$ = −2) due to reactions OH + O → H + O$_2$ and OH + O$_3$ → HO$_2$ + O$_2$. As O$_3$ reactions with OH are faster than with HO$_2$, only the rate determining steps (RDS) have been considered multiplied by two.

$^3$ Reactions XO + HO$_2$ → HOX + O$_2$, with X = Cl, Br and I, have been computed for each family with $\Delta$O$_3$ = −2 because the photolysis of HOX produces an additional O$_3$ loss by the OH radical (i.e. OH + O$_3$ → HO$_2$ + O$_2$). As these XO + HO$_2$ reaction are the rate limiting step, their loss rates have been multiplied by two.

families defined in Brasseur and Solomon (2005) with the inclusion of inorganic-driven O$_x$ chemical losses (IO$_x$ Loss). The direct O$_x$ loss rate (O$_x$ Loss) represents the major ozone depleting family within the tropical MBL and FT, while in the upper troposphere the HO$_x$ Loss cycles become the predominant loss processes up to the tropical tropopause. Within the MBL, and as a consequence of the increased inorganic iodine loading due to the direct oceanic injection of reactive I$_2$ / HOX species, IO$_x$ Loss cycles represent the second most important ozone-depleting family – IO$_x$ Loss $\approx$ 17 % (27 %) for Base (J$_{1,IO}$), respectively – surpassing in efficiency the contribution of HO$_x$ Loss. This additional source of inorganic iodine depends on the deposition of ozone on the ocean’s surface, and then acts as a natural buffer for ozone pollution in the lower troposphere: e.g. the warming effect of anthropogenic ozone in the global marine troposphere can be reduced by at least 3–10 % when inorganic iodine sources are considered (see Prados-Roman et al. (2014) for details). The negative geochemical feedback loop between anthropogenic ozone and oceanic inorganic iodine emissions proposed by Prados-Roman et al. (2014) exemplifies ocean biogeochemical cycles being affected by anthropogenic emissions. Comparatively, the overall effect of BrO$_x$+ClO$_x$ cycles constitute an ozone loss contribution smaller than 3 % in the MBL, reaching a percentage contribution > 10 % only in the upper troposphere. Note that our modelled daytime BrO levels averaged within the tropical MBL are ∼(0.2–0.3) pptv, with higher values of up to a few pptv calculated within coastal locations and regions of strong convection (Fernandez et al., 2014). Notably, the iodine impact on the acceleration of ozone loss cycles peaks in the UT (that is, within the extensive tropical ring of atomic iodine), with a maximum contribution to the total ozone loss of 0.06 (0.1) ppbv day$^{-1}$ (representing 14 (35) % of total loss) reached at 11 (13) km of altitude for the Base (J$_{1,IO}$) schemes, respectively. Our results indicate that, on average for the tropical troposphere, iodine-mediated ozone losses are responsible for at least 70–85 % of the total ozone depletion due to halogens.

The differences between IO$_x$ Loss and BrO$_x$–ClO$_x$ Loss contributions can be explained based on the higher reactivity
and therefore shorter lifetimes of iodine species: (i) due to the comparatively longer lifetimes of organic bromo- and chloro-carbons, inorganic bromine and chlorine cycles represent a major ozone loss process in the lower and middle stratosphere (Solomon et al., 1994; Salawitch et al., 2005); and (ii) the very fast catalytic reactions of iodine species make IO ozone loss cycles to be up to 10 times faster than BrO–ClO cycles for an identical Iy and Bry basis (i.e. $\text{IO}_x \text{Loss} / \text{I}_y \approx 10 \times \text{BrO}_x \text{–ClO}_y \text{Loss} / \text{Br}_y$). The total Iy abundance at the height where the relative IOx Loss maximizes (∼12 km) is in the range (0.66–0.81) pptv for the (Base–J1I03) schemes, while for bromine, Br12 km ≈ 1.0 pptv and Br17 km ≈ 3.0 pptv (Fernandez et al., 2014). This indicates that even when Bry abundances are larger in the upper troposphere, the greater O3 destruction efficiency of IOx makes iodine the dominant halogen contributing to tropospheric ozone loss throughout the tropics and mid-latitudes (see Table 6). Indeed, our results show that iodine-driven ozone loss cycles are the second most important ozone depleting family both in the tropical MBL and in the tropical and mid-latitude upper troposphere. Therefore we suggest that global models oriented to estimate past and future projections of tropospheric ozone burden and trends should include at least a simplified description of tropospheric iodine sources and inorganic chemistry, in addition to bromine.

Table 6 summarizes the integrated ozone column and the averaged ozone loss rate for different altitude intervals within the troposphere (MBL, FT, UT and total troposphere) within the tropical and mid-latitude regions. With the $J_{1I03}$ scheme, the total tropospheric O3 column is ∼1 DU smaller than for the Base scheme, representing an additional 4–7 % reduction of tropospheric ozone. Adding up the contribution of bromine and iodine from VSL sources, and gas and heterogeneous chemistry, the tropical tropospheric O3 column for the $J_{1I03}$ scheme is reduced by 2.6 DU relative to the NoVSL simulation, representing more than 10 % of the total tropospheric column. The vertical distribution of tropospheric ozone loss due to halogen chemistry within the tropics is very similar for both schemes considered here (25 % for the MBL, 65 % for the FT and 10 % for the UT). This indicates that most of the ozone loss due to iodine occurs in the free troposphere in agreement with previous estimates (Saiz-Lopez et al., 2012b).

Table 6 also presents the relative contribution of each of the odd oxygen families averaged at different altitude intervals and latitudinal bands. The overall impact of iodine chemistry on tropospheric ozone is larger in
Zonal annual average distributions of tropospheric ozone changes for different model schemes considering iodine and bromine VSL sources: (a) O$_3$ mixing ratios for the Base scheme (lower iodine loading); (b) difference between the higher and lower iodine schemes $\Delta$O$_3$($J_{I_x}$O$_y$ – Base); (c) impact of lower iodine with respect to only bromine chemistry $\Delta$O$_3$(Base – OnlyBr); (d) impact of considering only bromine chemistry relative to only long-lived sources $\Delta$O$_3$(OnlyBr – NoVSL). The colour scale represents 24 h mean model differences in ppbv, while the black contour lines show the percentage change between each pair of simulations computed as (A – B)/B × 100%.

4 Summary and conclusions

We propose the existence of a “tropical ring of atomic iodine” that circles the tropics with the sun. The tropical ring extends from 30° S to 30° N and maximizes at a height of 11–14 km, with volume mixing ratios ranging from 0.2 to 0.8 pptv. This photochemical phenomenon is driven by the fast photolysis rate of IO and the Arrhenius behaviour of the I$^+$ + O$_3$ reaction, and appears naturally in the upper troposphere where ambient temperatures minimize and ozone abundances are at least one order of magnitude below stratospheric levels. Within this tropical ring, noontime annual average I/IO ratios of ∼3 are modelled, reaching maximum values of ∼20 during events of vigorous convection. Inorganic iodine surpasses the contribution of organic VSL species throughout the troposphere, being CH$_3$I the dominant source that maintains I$_y$ levels in the FT and UT. Within the MBL and FT, HOI is the dominant I$_y$ species, both during the day and at night. The other abundant nighttime reservoirs are IONO$_2$ in the UT and the di-halogen molecules (I$_2$, IBr, and ICl) in the MBL.

Finally, we suggest that reducing uncertainties on the photochemistry of I$_x$O$_y$ species constitutes the main challenge to our current knowledge of atmospheric iodine chemistry. We show that if the photodissociation of I$_x$O$_y$ is neglected, then these higher oxides accumulate in the atmosphere due to their slow thermal decomposition and became an effective sink of active iodine in the FT and UT. Experimental and theoretical studies on the I$_x$O$_y$ photochemistry are required
to improve the knowledge on the inorganic iodine burden and its oxidative impacts in the troposphere. Based on our modelled range of inorganic iodine loading (0.7–1.0) pptv in the FT dependent on the consideration or not of I\textsubscript{x}O\textsubscript{y} photolysis, we show for the first time with a global model that iodine is the second most important ozone-depleting family in the tropical MBL and in the global marine UT, representing between (17–27) % and (11–27) % of the total ozone loss within each respective region. Therefore, we suggest global chemistry-climate models (CCMs) should include at least a simplified representation of iodine tropospheric chemistry for future CCM-Validation and CCM-Intercomparison projects concerned with tropospheric ozone over the oceans for past, present and future scenarios.

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