Iodine chemistry in the troposphere and its effect on ozone

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Abstract

Despite potential influence of iodine chemistry on the oxidizing capacity of the troposphere, reactive iodine distributions and their impact on tropospheric ozone remain nearly 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 $I_xO_y$ oxides (i.e., $I_2O_2$, $I_2O_3$ and $I_2O_4$) 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 ($IO_xLoss$) is 2–5 times...
larger than the combined bromine and chlorine cycles. When $I_xO_y$ photolysis is included, $IO_{x, \text{Loss}}$ represent 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 upper troposphere and in the tropical MBL. We suggest $i$) 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 ($CH_3I$) and other very short-lived (VSL) iodocarbons (e.g. $CH_2I_2$, $C_2H_5I$, $C_3H_7I$, $CH_2ICl$, $CH_2IBr$) 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 ($I_2$) 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 modeling studies and analysis of experimental data have suggested that the HOI/I$_2$ additional inorganic source must surpass the emission strength of organic VSL iodocarbons in order to reproduce observed iodine monoxide (IO) measurements over the open ocean environment (Jones et al., 2010; Mahajan et al., 2010, 2012; Gómez Martín et al., 2013b; Großmann et al., 2013; Lawler et al., 2014).

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 $IO_{x} = I + IO$. $IO_{x}$ 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 ($IOx_{\text{loss}}$, i.e. Chameides and Davis, 1980; Solomon et al., 1994; Vogt et al., 1999; McFiggans et al., 2000; Brasseur and Solomon, 2005) and changes to the HOx (i.e., $[\text{HO}_2]/[\text{OH}]$) and NOx (i.e., $[\text{NO}_2]/[\text{NO}]$) 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 ($I_xO_y$) 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 al., 2006; Saiz-Lopez et al., 2006; Huang et al., 2010; Mahajan et al., 2011; Atkinson et al., 2012).

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 (Puente du 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-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) modeling studies have suggested the potential important role of iodine in the destruction of tropospheric ozone. Additionally, recent studies have pointed out differences between ozonesonde climatologies and modeled $\text{O}_3$ abundances in the upper tropical troposphere (Young et al., 2013; 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$_2$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\(_x\)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. I\(_x\)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\(_x\)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) had been 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 1.9º (latitude) \(\times\) 2.5º (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\(_2\)BrCl, CHBr\(_2\)Cl and CHBrCl\(_2\)) and iodo- carbon presented there, extending the iodine inorganic chemistry mechanism. VSL oceanic sources of CH\(_2\)I\(_2\), CH\(_2\)ICl and CH\(_2\)IBr are based on parameterizations of chlorophyll-a satellite maps, including latitudinal variations between 50ºN–50ºS, a time dependent ice-mask for polar oceans and an annual seasonality (see Ordóñez et al. (2012) for details). The global CH\(_2\)IX (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 ~¼ 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 height over the oceans), 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 \((10 – 70) \times 10^7\) 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\(_2\)IBr 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\(_x\)O\(_y\) has been achieved only recently by means of photoionisation 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 et al., 2010), which rules out I\(_2\)O\(_5\) as nucleating species (Saunders and Plane, 2005). Some other iodine oxides with different I/O stoichiometry (\(x \neq 2\)) 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 were compiled from JPL-2010 (Sander et al., 2011) and IUPAC-2008 (Atkinson et al., 2007, 2008), and \(J\)-values are computed online considering both a look-up table and CAM-Chem actinic flux calculations (Lamarque et al., 2012). Sea-salt heterogeneous recycling reactions for HOI, IONO and IONO\(_2\) 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 higher iodine oxides is also proposed to proceed efficiently on sea-salt aerosols following the free regime approximation, although this additional sink of atmospheric iodine is a minor contributor compared to scavenging of I$_2$O$_3$ in water clouds. Table 4 presents the Henry Law’s coefficients ($k_H$) and 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 liquid droplets (SA$_{LIQ}$) and sea-salt aerosols (SA$_{SSLT}$) 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).

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

Prominent featureless absorption bands of I$_2$O$_y$ 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$_y$ 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 behavior 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 broad band absorption appearing under the IO spectrum to a single species (I$_2$O$_2$), Gómez Martín et al. (2005, 2007) obtained evidence of the same band resulting from an overlap of at least two different iodine oxides (I$_2$O$_2$ and I$_2$O$_3$). Here, in order to calculate atmospheric photolysis rates, we adopt for these two species 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$_3$ 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. Saunders, 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 iodosyl sulphate, which then, washed, converted to I$_2$O$_4$ (Daehlie and Kjekshus, 1964). Note
that the gas phase absorption spectrum of $I_2O_4$ 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 ($I_y$) has been defined as:

$$I_y = I + IO + HOI + IONO + I_xO_y + I_{\text{minor}} + I_{\text{dihal}}$$  \hspace{1cm} (1)

where for simplicity

$$I_xO_y = 2 \times (I_2O_2 + I_2O_3 + I_2O_4)$$  \hspace{1cm} (2)

$$I_{\text{minor}} = HI + OIO + INO_2 + INO$$  \hspace{1cm} (3)

$$I_{\text{dihal}} = 2 \times I_2 + IBr + ICl$$  \hspace{1cm} (4)

Two independent simulations were performed in order to estimate the range of $I_y$ loading and impact in the troposphere: the Base scheme and the $J_{I_xO_y}$ scheme. The Base scheme does not consider the photolysis of $I_xO_y$ oxides (i.e., $I_2O_2$, $I_2O_3$ and $I_2O_4$) and represents the lower $I_y$ loading limit. In this simulation $I_xO_y$ are decomposed back to IO$_x$ only by thermal decomposition, being removed from the gas phase via washout, uptake on sea-salt aerosols and dry deposition processes. The $J_{I_xO_y}$ scheme includes, in addition, the photolysis of $I_xO_y$, allowing for an efficient recycling of IO$_x$ in the gas phase within the troposphere. Therefore this second simulation represents the upper limit of tropospheric $I_y$ loading. Hereafter we use these two simulations to provide a range of reactive iodine loading, partitioning and distributions throughout the troposphere consistent with our current knowledge of iodine chemistry (within its uncertainties).

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 $I_xO_y$ was allowed ($J_{I_xO_y}$) 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 (SST) 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°N – 20°N) & (20°S – 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 hour 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, 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°E 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 and pmol/mol, 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$_2$I$_2$ and CH$_2$IBr in the MBL and (FT), respectively. Iodine-containing di-halocarbons are photolyzed 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 ($\theta_{cpt} \approx 380$ 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$_2$IBr and CH$_2$ICl 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 sources and chemistry (Jones et al., 2010; Mahajan et al., 2010; Gómez Martín et al.,
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$6.3x10$^3$ atoms cm$^{-3}$ s$^{-1}$) is an order of magnitude higher than that from all organo-iodine species combined ($5.7\times10^2$ atoms cm$^{-3}$ s$^{-1}$ at the surface level and totaling $\sim$1.0x10$^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$_y$ in the FT and UT is CH$_2$ICl, 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$_2$ICl is the di-halogen iodocarbon with the longest lifetime (~8 hours) 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$_2$ICl, 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$_y$ 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$_3$IX species increase: e.g. the iodocarbons, which are the VSL species with shortest
lifetimes, can temporally accumulate in the MBL 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 $I_xO_y$

The fast reactions IO+IO, IO+OIO and OIO+OIO lead to the formation of significant levels of $I_2O_2$, $I_2O_3$ and $I_2O_4$, respectively. As within the Base scheme only thermal decomposition and deposition onto background aerosol of iodine oxides are allowed, the levels of $I_xO_y$ build up in the atmosphere, reaching a total iodine abundance $> 1$ pptv in the FT and UT (Fig. 2C). If $I_xO_y$ were not photolabile they would represent 30% of the total $I_y$ 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 $I_xO_y$ 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 $I_xO_y$ species, hereafter, we present our best estimate of the upper and lower range of tropospheric iodine loading and its partitioning for the Base and $J_{I_xO_y}$ 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 $I_xO_y$ 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°N–20°S) for the Base and $J_{I_xO_y}$ 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 $I_y$ in the UT for the Base and $J_{I_xO_y}$ 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 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 (Puenteédura 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
$I_xO_y$ 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$_xO_y$ in the
UT; while for the $J_{I_xO_y}$ 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 $I_xO_y$ within the $J_{I_xO_y}$ 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 $I_xO_y$ (defined as
d[IO$_x$]/dt=−d[I$_xO_y$]/dt) is shown in Figure 4. Note that in Fig. 4 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 50 atoms I cm$^{-3}$ s$^{-1}$, within the MBL, and between
2 and 8 atoms I cm$^{-3}$ s$^{-1}$ in the tropical FT (Fig. 4A). As Base and $J_{I_xO_y}$ 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 3 orders
of magnitude larger than the contribution from $I_xO_y$ thermal decomposition (Fig. 4B), and
controls the tropospheric inorganic iodine burden. Due to the slow thermal breakdown of
higher oxides, $I_xO_y$ accumulate in the FT (Fig. 2C, see also Sect. 3.4). When the photolysis of
$I_xO_y$ is allowed, this process constitutes the most important source of reactive iodine in the
tropical free troposphere, recycling back more than 500 IO$_x$ molecules cm$^{-3}$ s$^{-1}$, and avoiding
a large $I_xO_y$ accumulation. As a consequence, larger amounts of IO$_x$ are maintained at higher
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$_y$ species from the MBL, sustained by stoichiometric 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-points height for the I$^-$IO ($\sim$ 7km), I$^-$HOI ($\sim$9 km) and IO$^-$HOI ($\sim$11 km) vertical noontime profiles occurs at the same altitude, regardless of the consideration or not of the photolysis of the I$_x$O$_y$ (see Fig 3A). This confirms that the steady state reached is nearly independent of the total amount of I$_y$ as expected due to the rapid photochemical time constants of the gaseous iodine system. The importance of constraining the absolute I$_y$ 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 $\sim$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$_y$ in the FT for the $J_{IxOy}$ 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’s law constant for HOI ($K_H^{HOI}$) has been adjusted between a more ($Base$) and less ($J_{IxOy}$) 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 $\sim$6–7 $\times$ 10$^7$ atoms (I) cm$^{-2}$ s$^{-1}$. For the $J_{IxOy}$ scheme, $\sim$95% of the wet-removal occurs in the MBL and FT and is controlled by the uptake on liquid droplets of HOI, IONO$_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 oxides accumulation. Note that from the overall I$_x$O$_y$ sinks, only $\sim$15% occurs due to irreversible deposition on sea-salt aerosols.

Within the $J_{IxOy}$ scheme, the IONO$_2$ abundance increases significantly above 10 km, representing the most abundant nighttime inorganic reservoir in the TTL (IONO$_2^{15km} = 0.4$ pptv) and the main sink of iodine at these heights. In the case of the $Base$ scheme, since less IO 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 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$_y$ species does not depend on the overall I$_x$O$_y$ or total I$_y$ 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 slowdown 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 30ºN to 30ºS (Fig. 5). Within this inhomogeneous tropical ring, annual zonal average atomic I peaks at 0.2 and 0.65 pptv for the Base and $J_{I_xO_y}$ schemes, respectively, accounting for up to 70% of the total annually-averaged I$_y$ in the tropics (black contour lines in Fig. 5). The altitude at which the maximum modeled 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 $J_{I_xO_y}$ 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 modeled 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 $J_{I_xO_y}$ schemes, respectively.

In both simulated schemes the atomic tropical ring and the relative I/I$_y$ 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$_y$ for
the Base scheme is at least halved with respect to the $J_{IyOy}$ scheme. If $I_yO_y$ species are not considered for the Base scheme, then the $I/I_y$ 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, etc.), the unusual feature of the halogen atom being 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, and 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 ~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 $J_{IyOy}$ 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 (~14–15 km or ~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 $J_{IxOy}$ schemes show a ratio enhancement from $I/IO \approx 3$ 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 $O_3$ 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 ppbv to 200 ppbv and from 250 K 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 $O_3$:

$$\frac{I}{IO} = \frac{J_{io}}{k_{io}, O_3}$$

(5).

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 $J_{IxOy}$ scheme calculates slightly smaller ratios because the assumed photochemical breakdown of $I_xO_y$ 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 $J_{IxOy}$ scheme are presented since the maximum values of both the iodine ring and the ratio are coincident in altitude when the photolysis of $I_xO_y$ 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 $O_3$ 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 30º N/S. Hence, we suggest 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 hs annual zonal average distribution of the main iodine species (besides atomic iodine) for the Base (left panels) and \( J_{Ixy} \) (right panels) schemes. With the exception of IONO\(_2\), which is the only species with a strong hemispheric gradient in the MBL due to the larger anthropogenic NO\(_x\) levels prevailing over the northern oceans, all inorganic iodine species abundances maximize within the tropical regions. IO abundance in the FT is reduced to \( \sim 1/3 \) 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 \( \geq 0.1 \) 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\(_3\)I. Above 7−8 km, and up to the tropopause, noon IO levels \( \geq 0.1 \) pptv can only be sustained by the combined release of iodine atoms from the photodissociation of CH\(_3\)I, whose concentration is \( \sim 0.1 \) pptv from 4 to 12 km, and the photolysis of I\(_2\)O\(_y\) that increases the lifetime of IO\(_x\) in the gas phase (see Fig. 4).

Fig. 8 shows that HOI is the dominant iodine species, representing more than 60% of total I\(_y\) between 1 and 8 km for the \( J_{Ixy} \) 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\(_2\)O\(_y\) 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\(_2\)O\(_y\), which turns out to be a non-reactive reservoir that does not recycle back to active IO\(_x\) (see gray shade in Fig.9A). Up to 70% of the total I\(_y\) is modeled to be transformed to unreactive I\(_2\)O\(_y\) 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\(_2\)O\(_y\) is assumed to be larger than that of HOI \( (k_{Ixy} > k_{HI}^{HOI}) \), 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 modeling experiment performed here indicates that either: i) an unrecognized removal processes for I\(_2\)O\(_y\) must exist in the FT and UT, ii) a substantial accumulation of unreactive I\(_2\)O\(_y\) prevails in the upper troposphere or iii) a decomposition pathway releasing active iodine, such as the
photodecomposition proposed in the $J_{I_xO_y}$ scheme, occurs. As to the authors knowledge there are no evidence for i) nor ii), we then suggest, based on experimental and theoretical studies (i.e. Gómez Martín et al., 2005; Saiz-Lopez et al., 2008) that the photochemistry of I$_x$O$_y$ should be further investigated in order to reduce uncertainties on the important chemical impacts of iodine chemistry. With the assumptions made in the $J_{I_xO_y}$ scheme, the I$_x$O$_y$ levels are clearly reduced in favor 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$_3$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 di-halogen 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 night time reaches 1.3 (1.7) pptv for the Base ($J_{I_xO_y}$) 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 abiotic 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 sheme, and 53%, 23% and 23% for the $J_{I_xO_y}$ scheme. Note that the contribution of 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 $J_{I\text{O}y}$ (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 $I_xO_y$ in the Base scheme, are clearly appreciated in Fig. 10. Note that even when the total inorganic loading for the $J_{I\text{O}y}$ 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 ~5 greater when $I_xO_y$ are photolysed. Indeed, if $I_xO_y$ are not considered when computing the total inorganic iodine (i.e., defining an equivalent magnitude $I_y^* = I_y - I_xO_y$), then the relative contributions $I/I_y^*$, IO/$I_y^*$ and HOI/$I_y^*$ for the Base scheme are equivalent to $I/I_y$, IO/$I_y$ and HOI/$I_y$ for the $J_{I\text{O}y}$ scheme. This confirms the rapid establishment of the photochemical steady state for the gaseous iodine system and the inert role of $I_xO_y$ on altering the $I_y$ partitioning for the Base scheme, thereby indicating that $I_xO_y$ 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 favors 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 IONO₂ 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 IₓOᵧ shows a flat diurnal concentration profile whereas in the JₓOᵧ scheme their daytime concentrations are negligible, due to efficient photolysis, and are only above pptv levels at night although at much lower abundances than IONO₂ and HOI. In both schemes the HOI photolysis dominates the early morning release of I atoms, compared to IONO₂, 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 IONO₂ in the ultraviolet (below 300nm) (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 IₓOᵧ in the Base scheme and the very rapid interplay between I and IO in the JₓOᵧ scheme dominate daytime Iₓ.

3.5 Implications for tropospheric ozone

Figure 12 presents the annual tropospheric ozone difference between the Base and JₓOᵧ schemes as a function of altitude and latitude. The O₃ changes increase from ~0.5 ppbv in the tropical MBL to up to ~2.5 ppbv in the UT of the mid-lats (Fig. 12B) following the increase of O₃ 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 ~5–6% for the SH due to the reduced impact of anthropogenic O₃ precursors, as compared to the NH. The (JₓOᵧ – Base) differences shown in Fig. 12B are of the same magnitude as those found between a pair of 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 IₓOᵧ) 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 ~5 km (400 – 500 hPa) is at least twice that of the simulation with only bromine chemistry, mostly in the free and upper troposphere. This all highlights the need for further experimental research on the photochemical characterization of IₓOᵧ.
Figure 13 presents the absolute (Fig. 13A) and relative (Fig. 13B) vertical range of ozone loss rate between the Base and \( J_{IaOy} \) 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 families defined in Brasseur and Solomon (2005) with the inclusion of iodine-driven \( O_x \) chemical losses (\( IOxLoss \)). The direct \( O_x \) loss rate (\( OxLoss \)) represents the major ozone depleting family within the tropical MBL and FT, while in the upper troposphere the \( HOxLoss \) 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 \( I_2/\text{HOI} \) species, \( IOxLoss \) cycles represent the second most important ozone depleting family (\( IOxLoss^{MBL} \approx 17\% \) (27\%) for Base (\( J_{IaOy} \)), respectively), surpassing in efficiency the contribution of \( HOxLoss \). 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 (\( J_{IaOy} \)) schemes, respectively. Our results indicate that, on average for the whole troposphere, iodine mediated ozone losses are responsible for at least 70–85\% of the total ozone depletion due to halogens.

The differences between \( IOxLoss \) and \( BrOx-ClOxLoss \) 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 IOx ozone loss cycles to be up to 10 times faster than BrOx-ClOx cycles for an identical Iy and Bry basis (i.e. \( IO_{\text{Loss}}/I_y \approx 10 \times ClO_{\text{Loss}}/Br_y \)). The total Iy abundance at the height where the relative \( IO_{\text{Loss}} \) maximizes (~12 km) is in the range (0.66–0.81) pptv for the \( (\text{Base}–J_{IyOy}) \) schemes, while for bromine, \( Br_y^{12\text{km}} \approx 1.0 \) pptv and \( Br_y^{17\text{km}} \approx 3.0 \) 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 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 summarises 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 \( J_{IyOy} \) scheme, the total tropospheric O3 column is ~1 DU smaller than for the \( \text{Base} \) 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 \( J_{IyOy} \) scheme is reduced by 2.6 DU relative to the \( \text{NoVSL} \) 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 the tropics than within the mid-latitudes, due to greater I/IO ratio and larger contribution of IOx to total inorganic iodine within the I atom tropical ring. Even when the change in the tropospheric ozone column between the \( J_{IyOy} \) and \( \text{Base} \) schemes is of similar magnitude for the tropics and the mid-latitudes (\( \Delta_{O3}^{\text{Tropics}} \approx -1.0 \) DU and \( \Delta_{O3}^{\text{Midlats}} \approx -1.1 \) DU), the ozone loss acceleration due to the increase in iodine loading is ~2
times larger for the $J_{IxOy}$ scheme within the tropics ($\Delta O3_{Loss}^{Tropics} \approx 26.2\ DU\ yr^{-1}$ and $\Delta O3_{Loss}^{Midlats} \approx 11.7\ DU\ yr^{-1}$). Our results indicate that the integrated contribution of the iodine system to the total rate of tropospheric ozone loss over the tropics is 2.2 (5.3) times larger than that of chlorine and bromine chemistry for the Base ($J_{IxOy}$) schemes, compared to a 1.2 (2.4) relative enhancement over the mid-latitudes. Notably, in the MBL iodine-mediated ozone loss rate is almost an order of magnitude faster than the combined rates of BrO$_x$ + ClO$_x$ cycles, even when the Base scheme is considered. Within the lower TTL, BrO$_x$-ClO$_x$ cycles result in higher ozone losses than IO$_x$ cycles only for the Base simulation. Note however that if photolysis of higher iodine oxides is allowed in the model, the IO$_x$ catalytic ozone depleting cycles continue to be more efficient than BrO$_x$-ClO$_x$ cycles throughout most of the TTL (Fig. 13).

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 30ºS to 30ºN and maximizes at a height of 11−14 km, with vmr ranging from 0.2 to 0.8 pptv. This photochemical phenomenon is driven by the fast photolysis rate of IO and Arrhenius behaviour of the I + O$_3$ reaction, and appears naturally in the upper troposphere where ambient temperature 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 night-time 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 in our modelled range of inorganic iodine loading
(0.7–1.0) pptv in the FT dependent on the consideration or not of I$_2$O$_5$ 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. 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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References


<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k / \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{I} + \text{O}_3 \rightarrow \text{IO} + \text{O}_2$</td>
<td>$2.1 \times 10^{-11} \text{e}^{(830/T)}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{IO} + \text{O}_3 \rightarrow \text{OIO} + \text{O}_2$</td>
<td>$3.6 \times 10^{16}$</td>
<td>2</td>
</tr>
<tr>
<td>$\text{I} + \text{HO}_2 \rightarrow \text{HI} + \text{O}_2$</td>
<td>$1.5 \times 10^{-11} \text{e}^{(-1090/T)}$</td>
<td>3</td>
</tr>
<tr>
<td>$\text{IO} + \text{NO} \rightarrow \text{I} + \text{NO}_2$</td>
<td>$7.15 \times 10^{-12} \text{e}^{(300/T)}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{IO} + \text{HO}_2 \rightarrow \text{HOI} + \text{O}_2$</td>
<td>$1.4 \times 10^{-11} \text{e}^{(540/T)}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{IO} + \text{IO} \rightarrow \text{OIO} + \text{I}$</td>
<td>$2.13 \times 10^{-11} \text{e}^{(180/T)} \times [1 + \text{e}^{(-p/191.42)}]$</td>
<td>1, 4</td>
</tr>
<tr>
<td>$\text{IO} + \text{IO} \rightarrow \text{I}_2\text{O}_2$</td>
<td>$3.27 \times 10^{-11} \text{e}^{(180/T)} \times [1 - 0.65 \text{e}^{(-p/191.42)}]$</td>
<td>1, 4</td>
</tr>
<tr>
<td>$\text{IO} + \text{OIO} \rightarrow \text{I}_2\text{O}_3$</td>
<td>$w_1 \cdot \text{exp} (w_2 \cdot T)^a$</td>
<td>4, 5, 6 $^g$</td>
</tr>
<tr>
<td>$\text{OIO} + \text{OIO} \rightarrow \text{I}_2\text{O}_4$</td>
<td>$w_1 \cdot \text{exp} (w_2 \cdot T)^b$</td>
<td>4, 5, 6 $^g$</td>
</tr>
<tr>
<td>$\text{I}_2 + \text{O} \rightarrow \text{IO} + \text{I}$</td>
<td>$1.25 \times 10^{-10}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{IO} + \text{O} \rightarrow \text{I} + \text{O}_2$</td>
<td>$1.4 \times 10^{-10}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{IO} + \text{OH} \rightarrow \text{HO} + \text{I}_2\text{O}_2 + \text{I}$</td>
<td>$1.0 \times 10^{-10}$</td>
<td>7</td>
</tr>
<tr>
<td>$\text{I}_2\text{O}_2 \rightarrow \text{OIO} + \text{I}$</td>
<td>$w_1 \cdot \text{exp} (w_2 / T)^c$</td>
<td>5, 6 $^g$</td>
</tr>
<tr>
<td>$\text{I}_2\text{O}_2 \rightarrow \text{IO} + \text{IO}$</td>
<td>$w_1 \cdot \text{exp} (w_2 / T)^d$</td>
<td>5, 6 $^g$</td>
</tr>
<tr>
<td>$\text{I}_2\text{O}_4 \rightarrow 2 \text{OIO}$</td>
<td>$w_1 \cdot \text{exp} (w_2 / T)^c$</td>
<td>5, 8 $^g$</td>
</tr>
<tr>
<td>$\text{I}_2 + \text{OH} \rightarrow \text{HOI} + \text{I}$</td>
<td>$1.8 \times 10^{-10}$</td>
<td>3</td>
</tr>
<tr>
<td>$\text{I}_2 + \text{NO}_3 \rightarrow \text{I} + \text{IONO}_2$</td>
<td>$1.5 \times 10^{-12}$</td>
<td>9</td>
</tr>
<tr>
<td>$\text{I} + \text{NO}_3 \rightarrow \text{IO} + \text{NO}_2$</td>
<td>$1.0 \times 10^{-10}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{OH} + \text{HI} \rightarrow \text{I} + \text{H}_2\text{O}$</td>
<td>$1.6 \times 10^{-11} \text{e}^{(440/T)}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{I} + \text{IONO}_2 \rightarrow \text{I}_2 + \text{NO}_2$</td>
<td>$9.1 \times 10^{-11} \text{e}^{(-146/T)}$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{HOI} + \text{OH} \rightarrow \text{IO} + \text{H}_2\text{O}$</td>
<td>$2.0 \times 10^{-13}$</td>
<td>10</td>
</tr>
<tr>
<td>$\text{IO} + \text{DMS} \rightarrow \text{DMSO} + \text{I}$</td>
<td>$3.2 \times 10^{-13} \text{e}^{(-925/T)}$</td>
<td>11</td>
</tr>
<tr>
<td>$\text{INO}_2 \rightarrow \text{I} + \text{NO}_2$</td>
<td>$1008 \times 10^{15} \text{e}^{(-13670/T)}$</td>
<td>12, 13, 14</td>
</tr>
<tr>
<td>$\text{IONO}_2 \rightarrow \text{IO} + \text{NO}_2$</td>
<td>$w_1 \cdot \text{exp} (w_2 / T)^f$</td>
<td>5, 15</td>
</tr>
<tr>
<td>$\text{INO} + \text{INO} \rightarrow \text{I}_2 + 2\text{NO}$</td>
<td>$8.4 \times 10^{-11} \text{e}^{(-2620/T)}$</td>
<td>3</td>
</tr>
<tr>
<td>$\text{INO}_2 + \text{INO}_2 \rightarrow \text{I}_2 + 2\text{NO}_2$</td>
<td>$4.7 \times 10^{-13} \text{e}^{(-1670/T)}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{OIO} + \text{NO} \rightarrow \text{IO} + \text{NO}_2$</td>
<td>$1.1 \times 10^{-12} \text{e}^{(542/T)}$</td>
<td>14</td>
</tr>
<tr>
<td>$\text{HI} + \text{NO}_3 \rightarrow \text{I} + \text{HNO}_3$</td>
<td>$1.3 \times 10^{-12} \text{e}^{(-1830/T)}$</td>
<td>16</td>
</tr>
<tr>
<td>$\text{IO} + \text{BrO} \rightarrow \text{Br} + \text{I} + \text{O}_2$</td>
<td>$0.30 \times 10^{-11} \text{e}^{(510/T)}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{IO} + \text{BrO} \rightarrow \text{Br} + \text{OIO}$</td>
<td>$1.20 \times 10^{-11} \text{e}^{(510/T)}$</td>
<td>1</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
I + BrO & \rightarrow IO + Br & 1.44 \times 10^{-11} & 17, 18, 19 \\
IO + ClO & \rightarrow I + OCIO & 2.585 \times 10^{-12} e^{(280/T)} & 1 \\
IO + ClO & \rightarrow I + Cl + O_2 & 1.175 \times 10^{-12} e^{(280/T)} & 1 \\
IO + ClO & \rightarrow IC1 + O_2 & 0.940 \times 10^{-12} e^{(280/T)} & 1 \\
IO + Br & \rightarrow I + BrO & 2.49 \times 10^{-11} & 18, 19 \\
IO + NO_3 & \rightarrow OIO + NO_2 & 9.0 \times 10^{-12} & 20 \\
IO + CH_3O_2 & \rightarrow CH_2O + I + HO_2 & 2.0 \times 10^{-12} & 2^b \\
CH_3I + OH & \rightarrow I + H_2O + HO_2 & 2.90 \times 10^{-12} e^{(-1100/T)} & 3 \\
I + NO_2 (+ M) & \rightarrow INO_2 (+ M) & k_0 = 3 \times 10^{-31} \times (T / 300)^1 & 3^i \\
I + NO_2 (+ M) & \rightarrow IONO_2 (+ M) & k_0 = 6.6 \times 10^{-11} & 3^i \\
I + NO (+ M) & \rightarrow INO (+ M) & k_0 = 6.5 \times 10^{-31} \times (T / 300)^{3.5} & 3^i \\
I + NO (+ M) & \rightarrow IONO (+ M) & k_0 = 7.6 \times 10^{-12} \times (T / 300)^{1.5} & 3^i \\
OIO + OH (+ M) & \rightarrow HOIO_2 (+ M) & k_0 = 1.8 \times 10^{-32} \times (T / 300)^1 & 3^i \\
& & k_e = 1.7 \times 10^{-11} & 3^i \\
& & k_e = 7.76 \times 10^{-10} \times (T / 300)^{-0.8} & 3^i
\end{align*}
\]

\hspace{1cm} 1 {\textsuperscript{1}} IUPAC-2008 (Atkinson et al., 2007); {\textsuperscript{2}} (Dillon et al., 2006b); {\textsuperscript{3}} JPL-2010 (Sander et al., 2011); {\textsuperscript{4}} (Gómez Martín et al., 2007); {\textsuperscript{5}} (Kaltsoyannis and Plane, 2008); {\textsuperscript{6}} (Gálvez et al., 2013); {\textsuperscript{7}} (Bösch et al., 2003); {\textsuperscript{8}} (Gómez Martín and Plane, 2009); {\textsuperscript{9}} (Chambers et al., 1992); {\textsuperscript{10}} (Chameides and Davis, 1980); {\textsuperscript{11}} (Dillon et al., 2006a); {\textsuperscript{12}} (McFiggans et al., 2000); {\textsuperscript{13}} (Jenkin et al., 1985); {\textsuperscript{14}} (Plane et al., 2006); {\textsuperscript{15}} (Allan and Plane, 2002); {\textsuperscript{16}} (Lancar et al., 1991); {\textsuperscript{17}} (László et al., 1997); {\textsuperscript{18}} (Bedjanian et al., 1997); {\textsuperscript{19}} (Gilles et al., 1997); {\textsuperscript{20}} (Dillon et al., 2008).

\hspace{1cm} 2^a w1= 4.687 \times 10^{-10} - 1.3855 \times 10^5 x e^{(-0.75 p / 1.62265)} + 5.51868 \times 10^{-10} x e^{(-0.75 p / 199.328)}

\hspace{1cm} 2^b w2 = -0.00331 - 0.00514 x e^{(-0.75 p / 325.687)} - 0.00444 x e^{(-0.75 p / 40.816)}

\hspace{1cm} 2^c w1 = 1.1659 \times 10^9 - 7.79644 \times 10^{10} x e^{(-0.75 p / 22.09281)} + 1.03779 \times 10^9 x e^{(-0.75 p / 568.15381)}

\hspace{1cm} 2^d w2 = -0.00813 - 0.00382 x e^{(-0.75 p / 45.575)} - 0.00643 x e^{(-0.75 p / 417.906)}

\hspace{1cm} 2^e w1 = 2.55335 \times 10^4 - 4.41888 \times 10^6 x 0.75 p + 85618600 x (0.75 p)^2 + 14218.81 x (0.75 p)^3

\hspace{1cm} 2^f w2 = -11466.82304 + 597.01334 x e^{(-0.75 p / 1382.62325)} - 167.3391 x e^{(-0.75 p / 43.75089)}

\hspace{1cm} 2^g w1 = -1.92626 \times 10^{14} + 4.67414 \times 10^{13} x 0.75 p - 3.68651 \times 10^8 x (0.75 p)^2 - 3.09109 x 10^6 x (0.75 p)^3

\hspace{1cm} 2^h w2 = -12302.15924 + 252.78367 x e^{(-0.75 p / 46.12733)} + 437.62868 x e^{(-0.75 p / 428.441)}

\hspace{1cm} 2^i w1 = -2.63544 \times 10^{13} + 4.32845 \times 10^{12} x (0.75 p) + 3.73758 \times 10^8 x (0.75 p)^2 - 628468.76313 x (0.75 p)^3

\hspace{1cm} 2^j w2 = -13847.85015 + 240.34465 x e^{(-0.75 p / 49.27141)} + 451.35864 x e^{(-0.75 p / 436.87605)}

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The empirical expressions of the form \( w_1 \cdot \exp ( w_2 \cdot T) \) were obtained by non-linear least squares fitting of Rice–Ramsperger–Kassel–Marcus (RRKM) theoretical results for the indicated reaction rate constants and thermal dissociation rates in the \((27 - 1013)\) hPa pressure range. RRKM calculations were carried out using the MESMER algorithm (Glowacki et al., 2012) as indicated in the corresponding references (e.g. Gálvez et al., 2013). Expression \( a \) produces negative values outside the range of modelled rate constants \((p < 20\) hPa), and therefore a fixed rate constant of \(3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) was assumed. Expressions \( e \) and \( f \) generate negligible dissociation rates below \(~500\) hPa which become negative at \(~8\) hPa – in this case they are set to zero below that pressure. Note that the parameterised pressure range of rate constants spans the atmospheric layer relevant for this work and beyond (see Figs. 3 and 4).

Updated heats of formation for IO, OIO, and \(\text{CH}_3\text{O}_2\) (Knyazev and Slagle, 1998; Dooley et al., 2008; Gómez Martín and Plane, 2009) show that the only accessible exothermic product channel of \(\text{CH}_3\text{O}_2 + \text{IO}\) (Drougas and Kosmas, 2007) is \(\text{CH}_2\text{O} + \text{I} + \text{O}_2\) \((\Delta H_r = -5 \pm 6 \text{ kJ mol}^{-1}\)), consistent with the high yield of I and low yield of OIO found experimentally (Bale et al., 2005; Enami et al., 2006). Sensitivity studies have been carried out using the preferred rate constant for this reaction of \(2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) (Dillon et al., 2006b), resulting in an enhancement of the ozone loss of \(0.5\%\) in the MBL and of less than \(0.1\%\) integrated throughout the troposphere in the \(J_{\text{H}_2\text{O}_2}\) scenario, and similarly negligible enhancements in the Base scenario. Impacts in the \(I_y\) partitioning are also very minor.

The temperature and pressure dependent rate constant \((k)\) is computed based on the low pressure \((k_0)\) and the high-pressure \((k_\infty)\) rate coefficients following JPL-2010 (Sander et al., 2011).

The Fast rate constants and a thermally stable product \(\text{HOIO}_2\) have been predicted theoretically (Plane et al., 2006), but no experimental studies reporting observation of \(\text{HOIO}_2\) and its photochemical properties in the gas phase are available. Since the level of uncertainty is even larger than for the \(I_x\text{O}_y\), it has not been included in the mechanism.
Table 2. Iodine chemistry scheme in CAM-Chem: Photochemical reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{3}I + h\nu \rightarrow CH\textsubscript{3}O\textsubscript{2} + I</td>
</tr>
<tr>
<td>CH\textsubscript{2}I\textsubscript{2} + h\nu \rightarrow 2I</td>
</tr>
<tr>
<td>CH\textsubscript{2}IBr + h\nu \rightarrow Br + I</td>
</tr>
<tr>
<td>CH\textsubscript{2}ICl + h\nu \rightarrow Cl + I</td>
</tr>
<tr>
<td>I\textsubscript{2} + h\nu \rightarrow 2I</td>
</tr>
<tr>
<td>IO + h\nu \rightarrow I + O</td>
</tr>
<tr>
<td>OIO + h\nu \rightarrow I + O\textsubscript{2}</td>
</tr>
<tr>
<td>INO + h\nu \rightarrow I + NO</td>
</tr>
<tr>
<td>INO\textsubscript{2} + h\nu \rightarrow I + NO\textsubscript{2}</td>
</tr>
<tr>
<td>IONO\textsubscript{2} + h\nu \rightarrow I + NO\textsubscript{3}</td>
</tr>
<tr>
<td>HOI + h\nu \rightarrow I + OH</td>
</tr>
<tr>
<td>IBr + h\nu \rightarrow I + Br</td>
</tr>
<tr>
<td>ICl + h\nu \rightarrow I + Cl</td>
</tr>
<tr>
<td>I\textsubscript{2}O\textsubscript{2} + h\nu \rightarrow I + OIO</td>
</tr>
<tr>
<td>I\textsubscript{2}O\textsubscript{3} + h\nu \rightarrow IO + OIO</td>
</tr>
<tr>
<td>I\textsubscript{2}O\textsubscript{4} + h\nu \rightarrow OIO + OIO</td>
</tr>
</tbody>
</table>

Photolysis rates are computed online considering the actinic flux calculation in CAM-Chem. The absorption cross-sections and quantum yields for all species besides the I\textsubscript{x}O\textsubscript{y} have been taken from IUPAC-2008 (Atkinson et al., 2007, 2008) and JPL-2010 (Sander et al., 2011).

\( ^a \) radical organic products are not considered.
\( ^b \) only the reaction channel reported in JPL 06-02 (Sander et al., 2006) is considered.
\( ^c \) photolysis reactions only considered in the \( J_{I\textsubscript{x}O\textsubscript{y}} \) 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>IONO₂ → 0.5 IBr + 0.5 ICl</td>
<td>γ = 0.01</td>
</tr>
<tr>
<td>INO₂ → 0.5 IBr + 0.5 ICl</td>
<td>γ = 0.02</td>
</tr>
<tr>
<td>HOI → 0.5 IBr + 0.5 ICl</td>
<td>γ = 0.06</td>
</tr>
<tr>
<td>I₂O₂ →</td>
<td>γ = 0.01§</td>
</tr>
<tr>
<td>I₂O₃ →</td>
<td>γ = 0.01§</td>
</tr>
<tr>
<td>I₂O₄ →</td>
<td>γ = 0.01§</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).

§ Deposition of IₓOᵧ species on sea-salt aerosols has been included following the free regime approximation.
Table 4. Iodine chemistry scheme in CAM-Chem: Henry’s Law constants and dry deposition velocities.

<table>
<thead>
<tr>
<th>Species</th>
<th>$k_0$ (M atm$^{-1}$)</th>
<th>Deposition velocity$^b$ (cm s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBr$^{ice}$</td>
<td>$2.4 \times 10^1$</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$^a$</td>
</tr>
<tr>
<td>HOI – ($J_{I\alpha O_y}$/ Base)</td>
<td>$1.9 \times 10^3$ / $4.5 \times 10^3$</td>
<td>0.75</td>
<td>1$^b$</td>
</tr>
<tr>
<td>IONO$_2^{ice}$</td>
<td>$1.0 \times 10^b$</td>
<td>0.75</td>
<td>2$^c$</td>
</tr>
<tr>
<td>INO$_2^{ice}$</td>
<td>$3.0 \times 10^{-1}$</td>
<td>0.75</td>
<td>1$^d$</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>I$_2$O$_2$</td>
<td>$1.0 \times 10^4$</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>I$_2$O$_3$</td>
<td>$1.0 \times 10^4$</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>I$_2$O$_4$</td>
<td>$1.0 \times 10^4$</td>
<td>1.0</td>
<td>2</td>
</tr>
</tbody>
</table>

$^8$ Dry deposition velocities are based on the THAMO model (Saiz-Lopez et al., 2008).

$^9$ Values reported in Sander (1999).

$^a$ Values based on the THAMO model (Saiz-Lopez et al., 2008).

$^b$ Considering a dissociation constant $K_a = 3.2 \times 10^9$ and a temperature dependent coefficient $c = 9800$ K

$^c$ Virtually infinite solubility is represented by using a very large arbitrary number.

$^d$ Value assumed to be equal to those of BrNO$_2$.

$^{ice}$ Species for which ice-uptake is considered following Neu and Prather (2012).
<table>
<thead>
<tr>
<th>Family</th>
<th>Reaction</th>
<th>$\Delta \text{O}_x$</th>
<th>Odd oxygen loss$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_x$</td>
<td>O + O$_3$ → 2×O$_2$</td>
<td>-2</td>
<td>$O_{x\text{Loss}} = 2\times R_{O+O_3} + R_{O1D+H2O}$</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$^\dagger$</td>
<td>$HO_{x\text{Loss}} = 2\times (R_{HO2+O} + R_{HO2+O_3})$</td>
</tr>
<tr>
<td></td>
<td>HO$_2$ + O$_3$ → OH + 2×O$_2$</td>
<td>-2$^\dagger$</td>
<td></td>
</tr>
<tr>
<td>$NO_x$</td>
<td>NO$_2$ + O → NO + O$_2$</td>
<td>-2</td>
<td>$NO_{x\text{Loss}} = 2\times (R_{NO2+O} + J_{NO3})$</td>
</tr>
<tr>
<td></td>
<td>NO$_3$ + hν → NO + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>$ClO_x+BrO_x$</td>
<td>ClO + O → Cl + O$_2$</td>
<td>-2</td>
<td>$ClO_{x\text{Loss}} =$</td>
</tr>
<tr>
<td></td>
<td>Cl$_2$O$_2$ + hν → 2×Cl + O$_2$</td>
<td>-2</td>
<td>$2 \times (R_{ClO+O} + J_{Cl2O2} + R_{ClO+ClO}^a + R_{ClO+ClO}^b + R_{ClO+HO2})$</td>
</tr>
<tr>
<td></td>
<td>ClO + ClO → Cl$_2$ + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ClO + ClO → Cl + OClO</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ClO + HO$_2$ → HOCl + O$_2$</td>
<td>-2$^\varepsilon$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BrO + O → Br + O$_2$</td>
<td>-2</td>
<td>$+ 2 \times (R_{BrO+O} + R_{BrO+BrO} + R_{BrO+HO2})$</td>
</tr>
<tr>
<td></td>
<td>BrO + BrO → 2×Br + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BrO + HO$_2$ → HOBr + O$_2$</td>
<td>-2$^\varepsilon$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BrO + ClO → Br + Cl + O$_2$</td>
<td>-2</td>
<td>$+ 2 \times (R_{BrO+ClO}^b + R_{BrO+ClO})$</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>$IO_{x\text{Loss}} = 2\times (R_{IO+O} + J_{IOO} + R_{IO+HO2})$</td>
</tr>
<tr>
<td></td>
<td>OIO + hν → I + O$_2$</td>
<td>-2</td>
<td></td>
</tr>
</tbody>
</table>
$\ IO + \ HO_2 \rightarrow HOI + O_2 \ -2\£$

\[
\begin{align*}
\IO + \ BrO & \rightarrow I + Br + O_2 \ -2 \ + 2\times(R_{\IO+BrO}^a + R_{\IO+ClO}^b + R_{\IO+ClO}^c) \\
\IO + \ ClO & \rightarrow I + Cl + O_2 \ -2 \\
\IO + \ ClO & \rightarrow ICl + O_2 \ -2 \\
\end{align*}
\]

$O_x = O(3P) + O(1D) + O_3 + NO_2 + 2\timesNO_3 + HNO_3 + HO_2NO_2 + 2\timesN_2O_3 + ClO + 2\timesCl_2O_2 + 2\timesOCIO + 2\timesCLONO_2 + BrO + 2\timesBrONO_2 + IO + 2\timesOIO + 2\timesIONO_2 + 2\timesI_2O_2 + 3\timesI_2O_3 + 4\timesI_2O_4$

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

$^\dag$HO$_x$ loss cycles represent a net change $2O_3 \rightarrow 3O_2 (\Delta O_x = -2)$ due to reactions $OH + O \rightarrow H + O_2$ and $OH + O_3 \rightarrow HO_2 + O_2$. As $O_x$ reactions with OH are faster than with HO$_2$, only the rate determining steps (RDS) have been considered multiplied by two.

$^\£$Reactions $XO + HO_2 \rightarrow HOX + O_2$, with $X = Cl, Br$ and $I$, have been computed for each family with $\Delta O_x = -2$ because the photolysis of HOX produces an additional $O_x$ loss by the OH radical (i.e. $OH + O_3 \rightarrow HO_2 + O_2$). As these $XO + HO2$ reaction are the rate limiting step, their loss rates have been multiplied by two.
Table 6. Integrated odd oxygen loss rates for each ozone depleting family within the troposphere.

| Simulation     |  
|----------------|--------------------------------------------------|
|                | Base                                             | $J_{iOy}$                                              |
|                | MBL     | FT    | UT   | Troposphere | MBL     | FT    | UT   | Troposphere |
| Tropics        |         |       |      |             |         |       |      |             |
| Ozone Column   | 1.31    | 13.68 | 9.01 | 24.18       | 1.23    | 13.11 | 8.73 | 23.25       |
| (DU)           |         |       |      |             |         |       |      |             |
| $\Delta O_3^{OnlyBr}$ (DU) | $-0.10$ | $-0.57$ | $-0.23$ | $-0.90$ | $-0.19$ | $-1.14$ | $-0.52$ | $-1.84$ |
| $\Delta O_3^{NoVSL}$ (DU) | $-0.15$ | $-1.01$ | $-0.51$ | $-1.66$ | $-0.24$ | $-1.58$ | $-0.79$ | $-2.59$ |
| Ozone Loss (DU yr$^{-1}$) | 111.39 | 505.94 | 36.38 | 666.29      | 117.98 | 520.75 | 42.32 | 692.51      |
| $O_x$ cycles (%) | 59      | 54    | 20   | 53          | 52      | 50    | 17   | 49          |
| $HO_x$ cycles (%) | 20      | 35    | 58   | 34          | 18      | 32    | 47   | 31          |
| $ClO_x$-$BrO_x$ (%) | 3       | 3     | 11   | 4           | 3       | 3     | 9    | 3           |
| $IO_x$ cycles (%) | 17      | 8     | 11   | 9           | 27      | 14    | 27   | 16          |
| Mid-Latitudes  |         |       |      |             |         |       |      |             |
| Ozone Column   | 1.91    | 17.85 | 10.64 | 30.66       | 1.83    | 17.19 | 10.29 | 29.57       |
| (DU)           |         |       |      |             |         |       |      |             |
| $\Delta O_3^{OnlyBr}$ (DU) | $-0.09$ | $-0.56$ | $-0.18$ | $-0.82$ | $-0.17$ | $-1.22$ | $-0.54$ | $-1.91$ |
| $\Delta O_3^{NoVSL}$ (DU) | $-0.16$ | $-1.22$ | $-0.52$ | $-1.90$ | $-0.24$ | $-1.88$ | $-0.87$ | $-2.98$ |
| Ozone Loss (DU yr$^{-1}$) | 73.66   | 351.68 | 29.35 | 471.36      | 75.39   | 358.19 | 33.03 | 483.05      |
| $O_x$ cycles (%) | 51      | 42    | 15   | 42          | 48      | 40    | 13   | 40          |
| $HO_x$ cycles (%) | 33      | 47    | 63   | 46          | 31      | 44    | 53   | 43          |
| $ClO_x$-$BrO_x$ (%) | 4       | 5     | 14   | 5           | 4       | 5     | 12   | 5           |
| $IO_x$ cycles (%) | 11      | 6     | 7    | 6           | 17      | 11    | 21   | 12          |

MBL: from the ocean surface up to ~900 m a.s.l. (~900 hPa). An ocean mask discarding grid-boxes above land was applied.

FT: from ~900 m (~900 hPa) to ~8.5 km (~350 hPa).

UT: from ~8.5 km (~350 hPa) to the model tropopause. Values above the model tropopause were not considered.

Tropics: (20ºN – 20ºS).
Midlats: (50°N – 20°N) & (20°S – 50°S).

\[ \Delta O_3^{OnlyBr} = O_3^{Iodine} - O_3^{OnlyBr} \], where \( Iodine \) is either Base or \( J_{I,xO_y} \) schemes for the left and right panels of the table, respectively, and \( OnlyBr \) is an equivalent simulation considering only bromine VSL sources. Analogously \( \Delta O_3^{NoVSL} = O_3^{Iodine} - O_3^{NoVSL} \), where \( NoVSL \) is a simulation where only long-lived bromine sources have been used (see text for details).
Figure 1. Absorption cross sections of the higher iodine oxides $I_xO_y$ ($x=2$, $y\geq2$). Gas phase experimental spectra tentatively assigned to $I_2O_2$ and $I_2O_3$ (Gómez Martín et al., 2005, 2007; Spietz et al., 2005) are plotted in blue and black respectively. The $I_2O_2$ spectrum has been smoothed by fitting a polynomial through it. The red line corresponds to the absorption spectrum of $I_2O_4$ in water (Russell Saunders, personal communication).
Figure 2. Vertical distributions of annually averaged organic and inorganic iodine species within the tropics (20°N–20°S): (A) organic VSL iodocarbons; (B) iodine atom released from different sources as a function of altitude, and (C) main I$_y$ species for the Base scheme. The abundance of I$_4$O$_y$ is shown by empty symbols. The horizontal line represents the approximate location of the tropical tropopause. 24 hours average profiles are shown in all cases.
Figure 3. Lower and upper limits of I$_y$ abundances within the tropical troposphere (20°N–20°S): (A) Main inorganic species at noon; (B) Major I$_y$ species at midnight. The lower limit corresponds to the Base scheme, while the upper limit is for the J$_{IOy}$ scheme.
Figure 4. Annual distribution of reactive iodine (IO\textsubscript{x} = I + IO) sources as a function of latitude and altitude: A) atomic iodine release from photolysis of CH\textsubscript{3}I; B) IO\textsubscript{x} production from thermal decomposition of I\textsubscript{x}O\textsubscript{y} for the Base scheme; C) Photodecomposition of higher oxides within the J\textsubscript{I\textsubscript{2}O\textsubscript{y}} scheme. Note that for B) and C), the photolysis of OIO to I + O\textsubscript{2} (Gómez Martín and Plane, 2009) is so efficient that the formation of OIO from I\textsubscript{x}O\textsubscript{y} (Table 1) is computed here as IO\textsubscript{x}. 24-h averages are shown in all cases.
Figure 5. The “tropical ring of atomic iodine” for the Base (top) and $J_{I_2O_y}$ (bottom) schemes:
(A,D) annual zonal average; (B,E) annual meridional average abundance of atomic I within the tropics (20°N–20°S); and (C,F) seasonal evolution of the zonally-averaged atomic I ring within the tropics. The color scale represents noontime volume mixing ratios (pptv) while black contour lines show the percentage contribution of atomic I to I$_y$. 
Figure 6A. Vertical profiles for the I/O ratio averaged over different regions and periods of time: (black) annual tropical (20°N–20°S) averages; (red) Western Pacific (WP) warm pool during February; (blue) at the midpoint of a strong convective cell within the WP region during a 3-day period in February. The upper and lower limits correspond to simulations with the Base and $J_{IO}$ schemes, respectively. Fig. 6B illustrates the vertical variation of $O_3$ abundances and temperature for each region and period of time.
Figure 7. Average annual noontime geographical distribution at 14 km of: A) atomic iodine, B) I/IO ratio, C) ozone and D) Temperature. The location of the WP region, also considered to compute the vertical profiles of Fig. 6, is outlined by the black rectangle.
Figure 8. Annual zonal average distribution of the main I$_y$ species in the troposphere for the Base (left) and $J_{H_2O}$ (right) schemes. The color scale represents 24-hs average volume mixing ratios (pptv) while black contour lines show the percentage contribution of each specie to I$_y$. 
Figure 9. Annual average tropical vertical partitioning of organic and inorganic iodine for the Base (left) and J1xOy (right) schemes, considering both daytime and nighttime (24-h) data. Minor organic and inorganic species have been lumped together for simplicity (see text for details).
Figure 10. Zonal additive distribution of main organic and inorganic iodine species at different altitudes for the Base (left) and $J_{IOy}$ (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_{I,Oy}** (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.
Figure 12. Zonal annual average distributions of tropospheric ozone changes for different model schemes considering iodine and bromine VSL sources: A) O$_3$ vmr for the Base scheme (lower iodine loading); B) difference between the higher and lower iodine schemes $\Delta O_3(J_{Ixy})_{h} - Base$; C) impact of lower iodine respect to 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 $\frac{(A-B)}{B} \times 100\%$. 
Figure 13. Modeled range of odd oxygen destruction for each of the ozone depleting families: (A) Annual total loss rates for the O\textsubscript{x}, HO\textsubscript{x}, BrO\textsubscript{x}-ClO\textsubscript{x} and IO\textsubscript{x} families within the tropical troposphere (20°N-20°S); (B) Percentage contribution of each family to the total loss rate for each scheme; (C) Vertical profiles of O\textsubscript{3}, NO\textsubscript{2}, OH and temperature within the tropics. Lower and upper limits of the range are for the Base and J\textsubscript{BrOx} schemes, respectively.