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Iodine's impact on tropospheric oxidants: a global model study in GEOS-Chem

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Abstract

We present a global simulation of tropospheric iodine chemistry within the GEOS-Chem chemical transport model. This includes organic and inorganic iodine sources, standard gas-phase iodine chemistry and simplified higher iodine oxide (I_2O_X, X = 2,3,4) chemistry, photolysis, deposition and parametrised heterogeneous reactions. In comparisons with recent Iodine Oxide (IO) observations the iodine simulation shows an average bias of $\sim +66\,\%$ available surface observations in the marine boundary layer (outside of polar regions), and of $\sim +73\,\%$ within the free troposphere ($350 <$ hPa < 900) over the eastern Pacific. Iodine emissions ($3.8\,\mathrm{Tg\,yr^{-1}}$) are overwhelmingly dominated by the inorganic ocean source, with 76 % of this emission from Hypoiodous acid (HOI). HOI is also found to be the dominant iodine species in terms of global tropospheric I_Y burden (contributing up to 70 %). The iodine chemistry leads to a significant global tropospheric O_3 burden decrease (9.0 %) compared to standard GEOS-Chem (v9-2). The iodine-driven O_X loss rate ($748\,\mathrm{Tg\,O_X\,yr^{-1}}$) is by photolysis of HOI (78 %), photolysis of OIO (21 %), and reaction of IO and BrO (1 %). Increases in global mean OH concentrations (1.8 %) by increased conversion of hydroperoxy radicals exceeds the decrease in OH primary production from the reduced O_3 concentration. We perform sensitivity studies on a range parameters and conclude that the simulation is sensitive to choices in parameterisation of heterogeneous uptake, ocean surface iodide, and I_2O_X (X = 2,3,4) photolysis. The new iodine chemistry combines with previously implemented bromine chemistry to yield a total bromine and iodine driven tropospheric O_3 burden decrease of 14.4 % compared to a simulation without iodine and bromine chemistry in the model. This is a significant impact and so halogen chemistry needs to be considered in climate and air quality models.

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1 Introduction

The chemistry of the troposphere controls the concentration of a range of climate gases including ozone (O_3) and methane (CH_4) (Kim et al., 2011; Voulgarakis et al., 2013; Young et al., 2013), and determines human and agriculture exposure to air quality pollutants such as O_3 and aerosols (Ainsworth et al., 2012; Fiore et al., 2012; Fowler et al., 2008). The chemical cycles maintaining concentrations of these atmospheric constituents are complex, and depend strongly upon the concentrations of O_3 and of the hydroxyl radical (OH) as key oxidants. Understanding the budgets and controls on these gases is therefore central to assessments of tropospheric chemistry (Voulgarakis et al., 2013).

The chemistry of O_3 and OH in the troposphere is coupled and the central aspects of this are well known (Young et al., 2013). The photolysis of O_3 produces an electronically excited oxygen atom ($O(^1D)$), which can react with a water molecule to produce two OH radicals. Subsequent reaction of OH with organic compounds (hydrocarbons, oxygenates, methane, carbon monoxide etc.) produces peroxy radicals (RO_2). If sufficient nitrogen oxide (NO) is available, the dominate fate of RO_2 radicals is to oxidise NO to nitrogen dioxide (NO_2), allowing the formation of O_3 via photolysis of NO_2 (Atkinson, 2000). Tropospheric O_3 also has a source via transport from the stratosphere, and is lost to the Earth's surface via dry deposition.

Over the last decades significant research effort has gone into understanding the production of O_3, typically over continental regions due to its adverse impact on health and food security (Ainsworth et al., 2012; Fowler et al., 2008). However less emphasis has been placed on its loss through chemical destruction. O_3 is chemically lost in the troposphere predominantly through its photolysis in the presence of water to produce OH. Secondary sinks include reaction with HO_2 or OH (Lelieveld and Dentener, 2000). Bromine and iodine compounds have also been identified as additional sinks for O_3 and as perturbations to OH cycling (Chameides and Davis, 1980; von Glasow et al., 2004). Of the two compounds iodine has arguably the more complex chemistry due to

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its many oxidation states, ability to form higher iodine oxides (I_2O_X, $X \geq 2$) and iodine particles (Saiz-Lopez et al., 2012b). There are significant uncertainties in iodine chemistry kinetics, and a rapidly evolving body of knowledge on iodine sources which we now describe.

Historically the dominant source of iodine in the atmosphere was thought to be iodinated organic compounds from the ocean. Initially methyl iodide (CH_3I) was considered the largest source but it was realised that even at the low observed concentration the very fast photolysis rates of other organo-halogens would lead to them playing a significant role (Chuck et al., 2005; Jones et al., 2010; Law and Sturges, 2006). More recently, emission of inorganic halogen compounds (I_2 and HOI) has been identified as a potentially significant flux of iodine into the atmosphere (Carpenter et al., 2013). This mechanism was originally proposed by Garland and Curtis (1981) whereby O_3 uptake to the ocean and the subsequent reaction with Iodide (I^-) leads to volatilisation of inorganic iodine from the ocean. Based on laboratory studies, fluxes of HOI and I_2 have been parameterised as a function of surface iodide concentration, O_3 concentration, 10 m wind speed and surface temperature (Carpenter et al., 2013; MacDonald et al., 2014).

Our understanding of the chemistry of iodine has been described in detail in recent publications (Saiz-Lopez et al., 2012b; Sommariva et al., 2012). Once emitted into the atmosphere, the highly labile iodinated precursors rapidly photolyse with lifetimes of seconds (e.g. I_2/HOI) to days (e.g. CH_3I) to release atomic iodine. The iodine can catalytically destroy O_3 by the reaction with of $O_3 + I$ to form IO, followed by secondary reactions (+HO_2, +IO, +NO_2, +BrO) which can regenerate atomic I without the abstracted oxygen. For instance IO reacts with HO_2, leading to HOI formation, and this is rapidly photolysed to reform I causing a net conversion of HO_2 to OH (Reaction R11).

A large body of experimental and theoretical work has been evaluated in JPL/IUPAC compilations (Atkinson et al., 2007, 2000; Sander et al., 2011). Whilst the key iodine reactions for processes of interest such as O_3 destruction (e.g. HOI, OIO photolysis) are now relatively well defined, the experimental rate data are limited or non-existent for

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certain processes. For example, I_2O_X ($X \geq 2$) photolysis cross-sections and quantum yields, heterogeneous uptake parameters and the ultimate chemical fate are all poorly quantified, yet these reactions can significantly affect the IO_X lifetime. I_2O_X ($X \geq 2$) forms through combination reactions (R1)–(R5) however questions remain about their polymerisation, photolytic properties and eventual fate as discussed further by Saiz-Lopez et al. (2012b). Recent work has shown some of the key iodine species to be well buffered to mechanism uncertainties, but highlights the sensitivity of iodine concentrations and hence atmospheric impacts of this higher oxide chemistry (Sommariva et al., 2012).

$$O_3 + I \rightarrow IO + O_2 \quad \text{(R1)}$$

$$IO + IO \rightarrow OIO + I \quad \text{(R2)}$$

$$IO + IO \rightarrow I_2O_2 \quad \text{(R3)}$$

$$IO + OIO \rightarrow I_2O_3 \quad \text{(R4)}$$

$$OIO + OIO \rightarrow I_2O_4 \quad \text{(R5)}$$

Due to their short lifetimes and low atmospheric concentrations measuring iodine species poses significant challenges and so the observational dataset is sparse. For decades, measurements have focused on organic compounds and mainly CH_3I (Saiz-Lopez et al., 2012b). Technique development for in-situ measurements has led to an increase in data availability over the last decade, for both organic (e.g. CH_3I and CH_2IX, with X = Cl, Br, I) and inorganic (e.g. IO, OIO, I_2) species (Saiz-Lopez et al., 2012b). Satellites may offer a mechanism to obtain global coverage, but retrievals at the low tropospheric concentrations are problematic (Schonhardt et al., 2008).

Recent organic and inorganic measurements from aircraft (Dix et al., 2013; Volkamer et al., 2015; Wang et al., 2015), balloons (Butz et al., 2009), mountain tops (Puentedura et al., 2012), ground stations (Lawler et al., 2014; Mahajan et al., 2010; Read et al., 2008) and cruises (Großmann et al., 2013; Jones et al., 2010; Mahajan et al., 2012) are establishing the global ubiquity of iodine compounds over the oceans. This increase in observations has enabled the development of global organic halogen emis-

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sions (Ordóñez et al., 2012) and more recently, datasets of IO observations with extensive geographical coverage (Prados-Roman et al., 2015b; Volkamer et al., 2015; Wang et al., 2015).

Although the increase in coverage and type of observations has somewhat improved constraints of iodine compounds, the recently suggested inorganic ocean source (HOI/I_2) required to reproduce observed concentrations of IO (Großmann et al., 2013; Gómez Martín et al., 2013; Jones et al., 2010; Mahajan et al., 2010) remains unconstrained by in-situ direct flux observations. However, observations of marine boundary layer I_2 concentrations have been made recently (Lawler et al., 2014). The inorganic emission requires knowledge of surface seawater iodide concentrations, but global iodide data remain spatially limited (Chance et al., 2014), and further complexities such as suppression of iodine emissions by dissolved organic matter also add uncertainty to the flux (Shaw and Carpenter, 2013).

Iodine chemistry has been evaluated by a number of box model studies (Sander et al., 1997; Mahajan et al., 2009; McFiggans et al., 2000, 2010; Read et al., 2008; Saiz-Lopez et al., 2007) and a few global model studies (Prados-Roman et al., 2015a; Saiz-Lopez et al., 2012a, 2014). The initial focus was predominantly on geographic regions with elevated concentrations (e.g. polar Sander et al., 1997; Saiz-Lopez et al., 2007 and coastal Mahajan et al., 2009; McFiggans et al., 2000; Saiz-Lopez et al., 2006) and attempted to explain localised chemical perturbations mainly through the use of box models. Iodine-driven O_3 loss was found to proceed through IO self reaction (Reactions R6–R8) at high IO concentrations (> 2 pptv),

$$O_3 + I \rightarrow IO + O_2 \quad \text{(R6)}$$

$$IO + IO \rightarrow OIO + I \quad \text{(R7)}$$

$$OIO + h\nu \rightarrow I + O_2 \quad \text{(R8)}$$

$$\text{Net: } 2O_3 \rightarrow 3O_2 \quad \text{(R9)}$$

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through HO_2 (Reactions R10–R12) at lower IO concentrations (Saiz-Lopez et al., 2012b),

$$O_3 + I \rightarrow IO + O_2 \quad \text{(R10)}$$
$$IO + HO_2 \rightarrow HOI + O_2 \quad \text{(R11)}$$
$$HOI + h\nu \rightarrow OH + I \quad \text{(R12)}$$
$$\text{Net: } O_3 + HO_2 \rightarrow OH + 2O_2 \quad \text{(R13)}$$

and by reactions between IO and BrO (Reactions R14–R17) where BrO concentrations are high.

$$O_3 + I \rightarrow IO + O_2 \quad \text{(R14)}$$
$$IO + BrO \rightarrow Br + I + O_2 \quad \text{(R15)}$$
$$\rightarrow Br + OIO \quad \text{(R16)}$$
$$OIO + h\nu \rightarrow O_2 + I \quad \text{(R17)}$$
$$\text{Net: } 2O_3 \rightarrow 3O_2 \quad \text{(R18)}$$

When considered alongside bromine chemistry, box model studies have shown the magnitude of these halogen driven O_3 loss processes to be up to 45 % (Mahajan et al., 2009; Read et al., 2008) of the total loss. Iodine can change the local $HO_2 : OH$ ratio due to the production of HOI from HO_2 and IO (Reaction R11), and its subsequent photolysis to release OH (Reaction R12) (Bloss, 2005; Chameides and Davis, 1980). Perturbation to the $NO : NO_2$ ratio has been shown to be significant at higher IO concentrations in polluted coastal locations (McFiggans et al., 2010) due to the ability of IO to oxidize NO into NO_2, which affects O_3 production. More recently, measurements in the marine boundary layer on ground-based island monitoring stations (Read et al., 2008; Mahajan et al., 2010; Gómez Martín et al., 2013), on ships (Großmann et al., 2013; Mahajan et al., 2010; Prados-Roman et al., 2015b), by balloon (Butz et al., 2009), and by aircraft (Dix et al., 2013; Volkamer et al., 2015; Wang et al., 2015) have demon-

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strated that these O_3 loss processes also occur in remote locations (e.g. non-coastal). These studies highlight the vertical and global extent of iodine chemistry.

Recently, the role of reactive halogens have also been investigated in global chemical transport models (Parrella et al., 2012) and chemistry-climate models (Ordóñez et al., 2012; Saiz-Lopez et al., 2014). A study considering only bromine chemistry reported significant impacts on OH concentrations and O_3 burdens with decreases of 4 and 6.5 %, respectively (Parrella et al., 2012). In a different study with a different model, inclusion of tropospheric bromine, iodine and chlorine chemistry led to topical tropospheric marine average O_3 columns to decrease on the order of 10 % (Saiz-Lopez et al., 2012a, 2014). As in the box model studies, up to ~ 30 % of the O_3 loss in the marine boundary layer (900 < hPa) is found to be driven by halogens (Saiz-Lopez et al., 2012a, 2014). Similarly, high levels of halogen-driven O_3 loss are also found in the upper troposphere (350 > hPa > tropospause), with lower (10–15 %) impacts in the free troposphere (350 < hPa < 900) (Saiz-Lopez et al., 2012a, 2014).

In this paper we present a global modelling study of tropospheric iodine chemistry, using the GEOS-Chem chemical transport model. The new chemistry is described in Sect. 2. Section 3 describes the comparison of modelled iodine concentrations against observations. Then Sect. 4 describes modelled global chemical distributions by family. Impacts on O_3 and OH are described in Sect. 5. In Sect. 6 we consider interactions of iodine with bromine, and in Sect. 7 we look at key sensitivities of the simulation. Section 8 summarises our conclusions.

2 GEOS-Chem simulation

We use here the GEOS-Chem (http://www.geos-chem.org) chemical transport model version v9-02, with transport driven by assimilated meteorological and surface data fields (GEOS-5) from NASA's Global Modelling and Assimilation Office (GMAO). We have adapted the existing chemistry scheme which includes O_X, HO_X, NO_X, and VOC chemistry as described recently in Mao et al. (2013), bromine chemistry (Parrella et al.,

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2012), and a mass-based aerosol scheme. Stratospheric chemistry is climatologically represented based on LINOZ McLinden et al. (2000) for O_3 and linearised chemistry is applied for other species with concentrations taken from the Global Modelling Initiative (GMI) as described previously Murray et al. (2012).

Iodine tracers (I_2, HOI, IO, OIO, HI, INO_2, INO_3, I, INO, CH_3I, CH_2I_2, CH_2IBr, CH_2ICl, I_2O_2, I_2O_3, I_2O_4 and "aerosol iodine") are included in the model. The modelled emissions, deposition, chemistry, photolysis and aerosol processes of these compounds are described below. No chemical processing of iodine species is performed in the stratosphere.

Notably our work differs from recent global iodine simulations (Saiz-Lopez et al., 2014) in its treatment of I_2O_X ($X = 2,3,4$). Our "standard iodine simulation" considers the photolysis of these compounds whereas their "Base" simulation does not. This leads to our simulations having a more active iodine chemistry and this is discussed in 2.4.

For budgets and general analysis we run the model at $2^\circ \times 2.5^\circ$ resolution for two years (2004–2006) discarding the 1st "spin up" year and using the final year (2005) for analysis and budgets. The model output is discussed with focus on the marine boundary layer (900 < hPa); the free troposphere (350 < hPa < 900); and upper troposphere (350 > hPa > tropopause). Comparisons with observations involve separate spun-up simulations, run with the date appropriate meteorology, sampled at the spatially and temporally nearest grid box.

2.1 Iodine emissions

Both organic and inorganic iodine species (Table 1) are emitted into the atmosphere. Organic iodine compounds (CH_3I, CH_2I_2, CH_2IBr, and CH_2ICl) are emitted from the monthly emissions of Ordóñez et al. (2012) which follows Bell et al. (2002) for CH_3I. Inorganic iodine compounds (HOI, I_2), formed from the uptake of O_3 to the ocean and the subsequent ocean surface reaction of O_3 with iodide (I^-), are emitted as calculated from Eqs. (19) and (20) in Carpenter et al. (2013). We parameterise ocean surface I^-

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concentration from the sea surface squared temperature relationship in Table 2 from Chance et al. (2014), the O_3 concentration in the bottom-most level of the model, and the 10 m wind speed from metrological fields.

Global emission totals (Table 1) are consistent with recent work (Saiz-Lopez et al., 2014) for organic iodine compounds as they also use Ordóñez et al. (2012). Inorganic fluxes calculated in this study are 32 % lower in previous work (Saiz-Lopez et al., 2014), despite using the same parameterisation (Carpenter et al., 2013; MacDonald et al., 2014). Although, model specific differences exist in sea surface temperatures, 10 m wind speeds and O_3 concentration the largest differences lie in the choice of parameterisation for sea surface iodide (see Sect. 7.5).

2.2 Iodine deposition

The model's deposition scheme has recently been updated (Amos et al., 2012). Dry deposition of the new iodine compounds is computed via the standard GEOS-Chem implementation of the "resistance-in-series" approach (Wesely, 1989) using literature Henry's law coefficients (Sander, 1999). This approach is applied to I_2, HI, HOI, INO_2, INO_3, I_2O_2, I_2O_3 and I_2O_4. Aerosol iodine is assumed to have the same deposition properties as sulfate aerosol.

Wet deposition is calculated for I_2, HI, HOI, INO_2, INO_3, I_2O_2, I_2O_3, and I_2O_4 for both large scale (frontal) and convection rain by applying scavenging in and below clouds (Liu et al., 2001) using species-specific values for Henry's law coefficients (Sander, 1999; Vogt et al., 1999) and molar heats of formation (Kaltsoyannis and Plane, 2008; Sander, 1999) as shown in Table 2. Fractionation between gas and liquid on ice is considered (Parrella et al., 2012; Stuart and Jacobson, 2003). Aerosol iodine is assumed to have the same deposition properties as sulfate aerosol.

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2.3 Iodine chemistry scheme

The gas phase iodine chemistry is shown in Tables 3 and 4. We include all iodine reactions presented by recent IUPAC (Atkinson et al., 2007, 2008) and JPL 10-6 (Sander et al., 2011) compilations relevant to the troposphere. Some additional reactions are included based on recent work (Sommariva et al., 2012; von Glasow et al., 2002) as justified in Sect. A1.1. Reactions within aerosol following uptake of species (HI, HOI, INO_2, INO_3) and processing of higher iodine oxides (I_2O_X, $X = 2,3,4$) after formation of I_2O_X are not treated explicitly but are parameterised as described in Sect. 2.5.

2.4 Photolysis rates

Photolysis reactions are summarised in Table 5. Photolysis rates are calculated online using the standard FAST-J code implementation in GEOS-Chem (Mao et al., 2010). Cross-sections are processed to the 7 wavelength bins used by FAST-J (Bian and Prather, 2002). For most cross-sections JPL 10-6 (Sander et al., 2011) values were used. For I_2O_X ($X = 2,3,4$) we assume the same absorption cross section as INO_3, an approach used previously (Bloss et al., 2010). For most species (I_2, HOI, IO, OIO, INO, INO_2, I_2O_2, CH_3I, CH_2I_2, CH_2IBr and CH_2ICl) we assume a quantum yield of 1, but for INO_3 we use a quantum yield of 0.21 (Sander et al., 2011).

2.5 Heterogeneous processes

In line with previous studies (McFiggans et al., 2000), we consider that the uptake of HOI, INO_2 and INO_3 leads to the recycling of iodine back into the gas phase as $\frac{1}{2}$ I_2 on sea-salt aerosol alone, whereas irreversible loss via uptake of HI leads to the generation of aerosol phase iodine. Uptake of I_2O_X ($X = 2,3,4$) also leads to the generation of aerosol phase iodine (on any aerosol). Heterogeneous uptake rates are computed using the GEOS-Chem standard code (Jacob, 2000) from reactive uptake coefficients

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(γ). Reactions considered and values of γ used are based on recommendations and previous studies (see Table 6 and Sect. A1.2).

2.6 Model bromine simulation

The bromine simulation in GEOS-Chem is described in Parrella et al. (2012) and bromine chemistry is included in the "standard simulation" throughout the paper. Parrella et al. (2012) presented a range of comparisons against satellite BrO observations. Although in general the model reproduces many of the features, there is a systematic underestimation of tropospheric BrO. New aircraft observations show that tropospheric BrO (Volkamer et al., 2015; Wang et al., 2015) may be higher than within our simulation. Our simulation also underestimates surface BrO observed in the tropical Atlantic marine boundary layer (hPa < 900) (~ 2 pptv, Read et al., 2008) by a ratio of ~ 5 (0.4 pptv). We consider the uncertainty in BrO concentration on our simulation as a part of our sensitivity study in Sect. 7.

3 Iodine model results and observation comparisons

In this section we describe and evaluate our iodine simulation. We initially focus on observational constraints for those iodine compounds that are directly emitted (Sect. 3.1), and then on the only secondary product which has been comprehensively observed (IO) (Sect. 3.2). We then turn to the averaged distribution of modelled iodinated compounds throughout the troposphere (Sect. 4).

3.1 Emitted iodine compounds

Figures 1 and 2 show annually averaged zonal (Fig. 1) and surface concentrations (Fig. 2) of organic and inorganic iodine precursors and their degradation products. These figures clearly illustrate the oceanic nature of iodine source species (CH_3I, CH_2I_2, CH_2ICl, CH_2IBr, HOI, I_2), with the highest concentrations over the tropical

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ocean. These plots also highlight the contribution of the included terrestrial CH_3I paddy field source (25 %) to global CH_3I concentrations from the Bell et al. (2002) emissions included in Ordóñez et al. (2012).

The emissions used here for organic iodine species have been assessed in (Ordóñez et al., 2012). We briefly present here a comparison between observations of CH_3I and CH_2ICl (Fig. 3) made during the UK Combined Airborne Studies in the Tropics (CAST) campaign over the tropical pacific (Guam) from January and February of 2014. These observations were made by gas chromatography mass spectrometry (GC-MS) as described in Andrews et al. (2015), using whole air samples from the Facility Airborne Atmospheric Measurement (FAAM) BAe 146-301 atmospheric research aircraft with techniques described in Andrews et al. (2013). The model shows an ability to capture the trend of decreasing concentration profile with height, but appears to underestimate the CH_3I concentrations (Fig. 3). Concentrations of CH_2ICl appear to be better simulated (Fig. 3). Although not definitive, this brief comparison suggests the model, if anything, underestimates the concentration of organic iodine.

The first in-situ remote open ocean I_2 concentration measurements were made at Cape Verde (Lawler et al., 2014). This dataset reported concentrations increasing between dusk and dawn in the range 0.2 to 1.7 pptv for the two separate measurement campaigns in May 2007 and May 2009 respectively. Our model captures the diurnal variation in I_2 of essentially zero during the day and increasing I_2 concentration during the night peaking just before dawn, but ranges between 2.5 and 7.5 pptv. Some component of this over estimate probably relates to the model's iodine heterogenous recycling which assumes 100 % conversion of HOI, INO_3, and INO_2 into $\frac{1}{2}$ I_2 rather than ICl and IBr which has been observed in laboratory studies (Braban et al., 2007).

3.2 Iodine oxide (IO) observations

Effectively, the only secondary iodine compound that has been observed and reported is IO. A comparison of a range of surface observations is shown in Fig. 4. Good agreement is seen in the West Pacific (TransBrom, Großmann et al., 2013) and tropical

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Atlantic at Cape Verde (Mahajan et al., 2010; Read et al., 2008), but the model has a generally high bias compared with other datasets (HALOCast-P, Mahajan et al., 2012; Malasapina, Prados-Roman et al., 2015b).

Biases between the daytime modelled and measured IO at Cape Verde and during the TransBrom cruise biases are within ∼ 22 and ∼ 16 % respectively. However, the model overestimates the Malasapina cruise IO concentrations (bias ∼ +50 to 250 %), and both under and over estimates values from the HALOCast-P cruise (bias ∼ −0.92 to 280 %). When all observations are latitudinally averaged (onto a 20° grid) a median bias of 66 % is found.

In Fig. 5 we show a comparison with recent aircraft IO observations from the TORERO campaign (Volkamer et al., 2015; Wang et al., 2015), which took place over the eastern Pacific. The model captures the vertical profile of IO but over estimates the observations (average bias of +82 % within the binned comparison). Biases in the comparison are greatest (bias = +125 %) in the marine boundary layer (hPa < 900) and lowest (bias = +73 %) in the free troposphere (350 < hPa < 900). The median bias in the upper troposphere (350 > hPa > tropospause) is +95 %.

From these comparisons it is evident that the model has some skill in simulating the average global surface distribution of IO (within a factor of 2) and similar skill at reproducing average vertical profiles. However, there is significant variability between locations, datasets and measurement groups. Increased global coverage, especially vertically, and inter-comparison of observational techniques are needed to better constrain the IO distribution.

4 Modelled distribution of iodinated compounds

We now analyse the modelled distribution of iodinated compounds. We start with the total gas phase inorganic iodine I_Y species ($2I_2 + HOI + IO + OIO + HI + INO + INO_2 + INO_3 + 2I_2O_2 + 2I_2O_3 + 2I_2O_4$) and then move to the distribution of the IO_X (I + IO) family.

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4.1 Total inorganic iodine (I_Y)

The modelled iodine system is schematically shown in Fig. 6. Iodine emissions total 3.8 Tg I yr^{-1} with most of this (3.2 Tg I yr^{-1}) coming from the inorganic source (84 %). This is comparable to the 83 % calculated by Prados-Roman et al. (2015b) (Ocean only, 60° N–60° S). Most (56 %) of the emissions occur in the tropics (22° S to 22° N). Our emissions which include inorganic emissions, compare with reported values of 1.8 Tg I yr^{-1} (Saiz-Lopez et al., 2012a) and 2.6 Tg I yr^{-1} (Saiz-Lopez et al., 2014) which also include an inorganic source.

Previous studies that did not consider an inorganic iodine source give values of 0.58 Tg I yr^{-1} (Ordóñez et al., 2012), and 0.65 Tg I yr^{-1} (Jones et al., 2010), consistent with our organic emissions. HOI represents the single largest source of oceanic iodine (76 %) with averaged oceanic emissions of 1.4×10^8 atoms (I) cm^{-2} s^{-1}. This value is towards the lower end of flux values required to reproduce IO observations in recent box modelling studies (Großmann et al., 2013; Jones et al., 2010; Mahajan et al., 2009).

Iodine deposition is predominantly through HOI (51 %). The remainder is mostly through deposition of INO_3 (20 %) and aerosol iodine formed by heterogeneous loss of gaseous iodine (HI, I_2O_X) (24 %). The majority of the deposition sink is back into the ocean (91 %). The global I_Y lifetime is 3.3 days but where depositional scavenging is weakest (upper troposphere, 350 > hPa > tropopause) this can increase by three orders of magnitudes.

Figures 7 and 8 show the average vertical and zonal distribution of iodine compounds through the troposphere. As expected given the surface source, the concentration of iodine drops with altitude. This drop is rapid across the top of the boundary layer. The concentrations of the short-lived source gases (CH_2IX and I_2) are negligible outside of the lowest model levels but the concentrations of others (CH_3I and HOI) persist further through the column. For CH_3I this is due to its longer lifetime of ∼ 4 days. However, the lifetime of HOI is shorter (∼ 4 min) and its persistence at higher altitudes reflects secondary chemical sources. From the top of the boundary layer to ∼ 10 km

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the I_Y profile is flat due to the rapid convective mixing within the tropics, however above this mixing zone the concentrations decrease. The inorganic iodine within the tropical (22° N–22° S) upper troposphere (> 10 km) is approximately equally sourced from upwards I_Y flux (6.6 Gg yr^{-1}) and organic iodine photolysis (7.9 Gg yr^{-1}), overwhelmingly of CH_3I. Overall, atmospheric iodine is dominated by three IOy species (HOI, IO, and INO_3) with HOI representing the greatest fraction (~ 70 %) in the free troposphere (350 < hPa < 900).

4.2 The iodine oxide family: IO_X (I + IO)

Globally IO_X production is dominated by inorganic iodine I_Y photolysis (HOI, 76 %; OIO, 11 %). The major loss route for IO_X is HOI production through IO reaction with HO_2 (Reaction R11, 77 %), with additional loss routes through self-reaction, reaction with NO_X, and BrO contributing 10, 7.7, and 4.6 % respectively.

The global average IO_X lifetime with respect to chemical loss is ~ 1 min, but increases within the tropical upper troposphere (350 > hPa > tropopause) (up to 9 times) and beyond latitudes of 80° N and S (up to 4 times) due to colder temperatures. The major IO formation route (I + O_3) slows in these regions due to colder temperatures. This moves the partitioning of IO_X from IO to I. As the IO_X loss routes proceed predominantly through IO, the overall IO_X lifetime increases. This causes an increase in the annually averaged I to IO ratio which peaks with a ratio of 0.7–1.4 within the tropical upper troposphere (350 > hPa > tropopause). This is at the lower end of the daytime range of 1–4 previously calculated (Saiz-Lopez et al., 2014). As described in Sect. 4.1, the I_Y (and thus the IO_X) in this region is approximately evenly sources from photolysis of transported organic iodine species and direct transport of I_Y.

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5 Impact of iodine on O_3 and OH

O_3 and OH are two key parameters for climate and air quality. Previous studies (Bloss et al., 2005; Saiz-Lopez et al., 2008, 2012a) have identified significant impacts of iodine on these compounds. Here we compare our model predictions to available observational constraints and then diagnose the model change.

5.1 Impact on O_3

On inclusion of iodine, the calculated global tropospheric O_3 burden drops from 367 to 334 Tg (9.0 %). Figure 9 shows the annual average tropspheric column, surface and zonal change in O_3. On average the O_3 burdens in the marine boundary layer (900 < hPa) decreased by 19.5 %, by 9.8 % the free troposphere (350 < hPa < 900), and 6.2 % in the upper troposphere (350 > hPa > tropospause). The decrease is greater in the Southern Hemisphere (9.5 %), than the Northern Hemisphere (8.5 %).

Surface (lowest most model level) O_3 shows an average decrease of 3.5 ppbv globally, with large spatial variability (Fig. 10) and greater decrease over the oceans (21 %) than the land (7.3 %). Comparing against the Global Atmospheric Watch (GAW, Sofen et al., 2015) surface O_3 observations (Fig. 10), there is no obvious decrease in the ability of the model to capture seasonality in surface O_3 although there is systematic decrease in O_3 concentration with the inclusion of iodine.

Figure 11 shows a comparison between a selection of annually averaged O_3 sonde profiles for the same year (2005, World Ozone and Ultraviolet Data Centre WOUDC, 2014) and our model simulation with and without iodine. A decrease in O_3 concentration is evident throughout the troposphere (average of 3.1 ppbv). As with comparison of surface observations (Fig. 11), no clear decline in model skill at capturing annual sonde profiles is apparent on inclusion of iodine, with some locations improving and others degrading. An exception to this is O_3 observations greater than 60° S at the surface where bias are increased and in the tropical free troposphere (350 < hPa < 900) where model O_3 biases are decreased.

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5.2 O_3 budget

We diagnose the impact of iodine on O_3 by calculating the model's tropospheric odd oxygen budget in Table 7. Here we define O_X as $O_3 + NO_2 + 2NO_3 + PAN + PMN + PPN + HNO_4 + 3N_2O_5 + HNO_3 + BrO + HOBr + BrNO_2 + 2BrNO_3 + MPN + IO + HOI + INO_2 + 2INO_3 + 2OIO + 2I_2O_2 + 3I_2O_3 + 4I_2O_4$.

Iodine provides a global tropospheric O_X loss of $\sim 750\,Tg\,yr^{-1}$ (15 % of the total). This is significantly larger than the $184\,Tg\,yr^{-1}$ from bromine chemistry and is comparable to the sink from the $O_3 + OH$ reaction. Overwhelmingly this loss is from the photolysis of HOI after its production from the reaction of IO with HO_2. The O_3 production term increases slightly (~ 1 %) with the inclusion of iodine reflecting small changes in the total reactive nitrogen (NO_Y) partitioning.

Iodine induced O_3 loss within the marine (land mask applied and between 50° N–50° S) troposphere of $\sim 540\,Tg\,yr^{-1}$ is comparable to previous reported values Saiz-Lopez et al. (2014) when I_2O_X ($X = 2,3,4$) photolysis is included ($\sim 500\,Tg\,yr^{-1}$).

Figure 12 shows the relative importance of different O_X sinks in the vertical. The "classical" O_3 loss routes ($h\nu + H_2O$, HO_X) dominate; however within the boundary layer and the upper troposphere (350 > hPa > tropopause), iodine represents 33 and 26 % of the total loss, respectively. The loss within the marine boundary layer (900 < hPa) in this study is again comparable to values reported recently of 28 % (Prados-Roman et al., 2015a). This decreases rapidly with increasing altitude within the lower troposphere to values closer to 10 % reflecting the lower of IO concentrations (see Figs. 7 and 8). In the upper troposphere, higher IO_X and BrO_X concentrations lead to increased loss of O_3.

Figure 13 shows the zonal variation in the different O_X destruction terms (in terms of the O_X lifetime). It is evident that, in the model, iodine destruction is more spatially prevalent than bromine destruction, which is confined predominantly to the Southern Ocean. The impact of iodine is hemispherically asymmetric reflecting the higher NO_X in the Northern Hemisphere, higher BrO concentrations in the southern oceans and the

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larger ocean area in the Southern Hemisphere increasing emissions. Convective transport in the tropics rapidly lifts iodine species into the free troposphere (350 < hPa < 900) where they can destroy O_3.

5.3 Impact on OH

Previous box model studies which investigated impact of iodine on OH concentration in the Antarctic (Saiz-Lopez et al., 2008), mid-latitude coastal (Bloss, 2005), tropical marine regions (Mahajan et al., 2010), and the free troposphere (Wang et al., 2015) found increases in the OH concentration due to IO enhancing conversion of HO_2 to OH. However we find that the inclusion of iodine in the model has little impact on the global mean OH concentrations. It slightly increases from 12.2 to 12.5×10^5 molec. cm^{-3} (1.8 %). This small increase is surprising given the 12 % reduction in the primary source ($O_3 + H_2O + h\nu$) due to lower O_3 concentrations. However, this is to some extent, compensated for by an increase in the rate of conversion of HO_2 to OH by IO. Previous studies using constrained box models (Bloss, 2005; Saiz-Lopez et al., 2008) could not consider this impact on the primary production of OH and it appears from our simulation that the overall impact is lower than previously thought.

6 Combined impact of bromine and iodine

The importance of halogen cross-over reactions (BrO + IO) for O_3 loss has been previously highlighted and found to be required to replicate observed diurnal surface O_3 loss in the marine boundary layer (Read et al., 2008). To explore these interactions a further two runs were performed: one simulation with iodine but without bromine ("just iodine") and one without any halogens ("no hal").

Global tropospheric burdens of are 390, 367 (reduction of 5.9 %), 357 (8.5 %) and 334 Tg (14 %) for the simulations without halogens ("no ha"), with just bromine ("standard simulation"), with just iodine ("just iodine"), and with both iodine and bromine

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chemistry ("iodine simulation") respectively. The sum of the changes in O_3 burden for the runs considering halogens individually is very slightly lower (0.1 %) than when considered simultaneously.

Figure 14 shows the combined daily surface loss rate of O_3 driven by bromine and iodine (upper panel). This correlates with IO concentrations (Fig. 2) reflecting iodine's role in marine boundary layer O_3 destruction. Figure 14 also shows modelled and observed fractional diurnal fractional O_3 change at Cape Verde in the remote marine boundary layer (lower panel). The diurnal change is calculated by subtracting each day's maximum O_3 mixing ratio from hourly observations (2006–2012, Sofen et al., 2015). Each value is then divided by the mean value for that day to give a fractional change, then this is presented averaged by hour over all the observations. The simulation's fidelity increases significantly with the inclusion of iodine (Fig. 14) but there is little impact from bromine. Whereas modelled IO concentrations at Cape Verde shows agreement with observations (Fig. 4), BrO concentrations (~ 0.4 pptv) are significantly lower than reported (~ 2 pptv, Read et al., 2008). This underestimate of BrO in the model is a systemic problem (see Sect. 2.6) and so model estimates of the impact of Br on atmospheric composition described here are probably an underestimate.

Global mean tropospheric concentrations of OH are 12.80, 12.24, 13.02, and 12.47×10^5 molecules cm^{-3} for the simulations without halogens ("no hal"), with just bromine ("standard simulation"), with just iodine ("just iodine"), and with both iodine and bromine chemistry ("iodine simulation") respectively. OH shows a differing response to bromine and iodine chemistry. As discussed in Sect. 5.3, inclusion of iodine leads to a small increase in OH concentrations. When solely iodine is considered, OH concentrations increase by 1.8 % compared to when no halogens are included. Whereas bromine chemistry leads to a reduction in OH (4.3 %), as reported previously (Parrella et al., 2012), due to enhanced production by HOBr photolysis not compensating for a decrease in the primary OH source ($O_3 + H_2O + h\nu$) from a reduced O_3 burden. The net impact overall on inclusion of halogens is a global reduction in OH (2.6 %).

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In our simulations, the global impact of Br and I chemistry are essentially additive with apparently limited impact from the cross reactions. The global impact of iodine appears significantly larger than that of bromine, however, given that the model underestimates the concentrations of Br compounds this should be subject to future study.

7 Sensitivity studies

As discussed in the introduction, a range of uncertainties exist in our understanding of tropospheric iodine. We perform sensitivity analysis on some of these parameters using the $4^\circ \times 5^\circ$ version of the model. We chose to analyse the sensitivity to inclusion of inorganic iodine emissions, heterogeneous loss and cycling, photolysis rates and ocean surface iodide. Values are quoted as a % change from the iodine simulation described in Sects. 2–5. Figure 16 summarises the fractional impact of these experiments on the globally averaged vertical distribution of I_Y, O_3 and vertical profile comparison of observations of IO from the TORERO campaign (Volkamer et al., 2015; Wang et al., 2015). Additional information is listed in Table A1 in the Appendix A.

7.1 Just Organic Iodine

Until recently many studies solely considered organic iodine (Jones et al., 2010; Ordóñez et al., 2012) emissions. As discussed in Sect. 3.1, our simulation uses the Carpenter et al. (2013) inorganic emission parameterisation as well as organic iodine emissions from Ordóñez et al. (2012). When we just consider organic iodine emissions ("Just org. I") we find that global I_Y burdens decrease ($\sim 65\,\%$), and mean surface marine boundary layer ($900 < \mathrm{hPa}$) IO decreases ($\sim 83\,\%$). The median bias against TORERO IO observations decreases by $\sim 68\,\%$ and becomes a negative bias of $-25\,\%$. The decreased I_Y leads to the mean global OH decreasing by 0.64 % and global tropospheric O_3 increasing by 5.5 %.

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7.2 Heterogeneous uptake and cycling

There is limited experimental data for the reaction probability (γ) for iodine species on aerosol. Our base case scheme follows the literature precedent (McFiggans et al., 2000) and assumes heterogeneous recycling of unity (e.g. HOI = $\frac{1}{2}$ I_2) on sea salt which is not limited by aerosol acidity. However, the acidity of aerosol may limit iodine cycling as not all sea-salt aerosols are acidic (Alexander, 2005) and other aerosols may irreversibly uptake iodine. Detail on the reaction probabilities (γ) chosen is in Appendix A. To explore these uncertainties four simulations were run: (1) with the γ values that led to I_2 release doubled ("het. cycle ×2"), (2) with the γ values halved ("het. cycle /2"), (3) with all uptake reactions leading to a net loss of iodine ("No het. cycle"), and (4) a run where sulfate aerosol leads to a sink for iodine with the same γ values as for sea salt ("Sulfate uptake").

Increasing the heterogeneous cycling ("het. cycle ×2") converts more HOI (the dominant I_Y species) into I_2, thus reducing the rate of HOI deposition. The global I_Y burden increases by ∼ 6 %, mean surface marine boundary layer (900 < hPa) IO concentration increases by ∼ 2 % and the median bias with respect to the TORERO IO observations increases by ∼ 26 to 100 % (Fig. 16). Decreasing the heterogeneous cycling ("het. cycle /2") has the opposite impact of roughly the same magnitude. Global average I_Y burden decreases (∼ 4.3 %), average surface marine boundary layer IO decreases (∼ 1.8 %) and the median bias with respect to the TORERO IO observations decreases (∼ 18 %) to 66 %.

The impacts of theses changes is small overall. Increased iodine cycling leads to a decrease in the tropospheric O_3 burden of ∼ 0.69 % and global mean OH increases by ∼ 0.05 %, whereas decreased cycling leads to the tropospheric O_3 burden increasing by ∼ 0.56 % and OH decreasing by ∼ 0.09 %.

By removing the release of I_2 to the gas-phase following uptake of iodine ("no het. cycle") or by considering irreversible iodine loss to sulfate aerosol ("Sulfate uptake") the global I_Y burdens decrease significantly by 47 and 48 %, respectively. Surface marine

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boundary layer (900 < hPa) IO concentration decreases by 48 and 22 %. The median bias with respect to the TORERO IO observations decreases in the case of "no het. cycle" (∼ 84 %) to 13 % and decreases in "Sulfate uptake" (∼ 92 %) to −6.7 %. The "Sulfate uptake" scenario shifts the median bias with the TORERO IO observations to be negative, instead of positive (∼ +80 % for the base iodine simulation at 4 × 5).

This large decrease in I_Y decreases the potency of iodine chemistry. The reductions in the tropospheric O_3 burdens (4.1 and 4.5 % for "no het. cycle" and "Sulfate uptake") are comparable to the simulation where only organic iodine sources are considered (5.5 %, "Just I Org."). Global mean OH decreases slightly by ∼ 0.54 and ∼ 0.87 % under these two scenarios. These two sensitivity runs represent large perturbations to the iodine system, highlighting the importance and uncertainties in heterogeneous chemistry.

7.3 Uncertainties in photolysis parameters

Absorption cross-sections and quantum yields for iodine species are few and their temperature dependencies are not known. Notably, the absorption cross sections for the higher iodine oxides (I_2O_2, I_2O_3, I_2O_4) are highly uncertain (Bloss et al., 2001; Gómez Martín et al., 2005; Spietz et al., 2005) and we use the INO_3 spectrum in our simulation. This uncertainty was tested in 3 simulations: (1) absorption cross-sections were doubled ("I_2O_X X-sections ×2"), (2) tentative literature assignments of spectra were used for I_2O_3 and I_2O_2 (Bloss et al., 2001; Gómez Martín et al., 2005; Spietz et al., 2005), with I_2O_2 used for I_2O_4, (3) and finally no I_2O_X photolysis at all was considered ("No I_2O_X photolysis").

Sensitivity runs "I_2O_X X-sections ×2" and "I_2O_X exp. X-sections" increase photolysis rates, therefore resulting in an increase in the I_Y lifetime of 5.3 and 8.3 % and the I_Y burdens by 3.1 and 4.8 % respectively. The average surface marine boundary layer (900 < hPa) IO concentration responds by increasing by 4.3 and 6.7 % for "I_2O_X X-sections ×2" and "I_2O_X exp. X-sections" respectively. Both these simulation increase median bias with TORERO IO observations by ∼ 4.8 to 84 % and ∼ 7.6 to 86 %, re-

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spectively. The impacts on O_3 burden are small with a decrease of 0.4 and 0.6 % for "I_2O_X X-sections ×2" and "I_2O_X exp. X-sections" respectively. Global mean OH concentrations increase by 0.05 and 0.09 % respectively.

The removal of I_2O_X ($X = 2,3,4$) photolysis reduces the global tropospheric I_Y burden (∼ 35 %), reduces surface marine boundary layer (900 < hPa) IO (∼ 40 %), increases tropospheric O_3 burden (5.1 %) and decreases global mean OH (0.9 %) with respect to the base iodine simulation. The median bias with respect to the TORERO IO observations becomes negative and decreases by ∼ 81 to 16 %, illustrating a large change in the simulated IO profile by removing the I_2O_X photolysis (Fig. 16). This was also noted by Prados-Roman et al. (2015b) with respect to surface observations.

Our "No I_2O_X photolysis" simulation is akin to the "base" simulation of (Saiz-Lopez et al., 2014). This was presented as a lower bounds for iodine chemistry. Their "JI_XO_Y" simulation is akin to our iodine simulation. Saiz-Lopez et al. (2014) find a decrease in marine tropospheric O_3 column burden of 3.0 and 6.1 % compared to a simulation with no iodine chemistry for their "base" and "JI_XO_Y" simulations respectively. Considering the same domain our comparable simulations show values of 4.0 to 8.7 %.

7.4 Marine boundary layer BrO concentration

As discussed in the introduction and Sect. 6, bromine and iodine chemistry are coupled. GEOS-Chem appears to underestimate BrO (Parrella et al., 2012), with for example, our simulation underestimating the BrO concentrations at Cape Verde (Read et al., 2008) (∼ 2 pptv) by a factor of ∼ 5.

To test the sensitivity of the model to BrO concentrations, a simulation with BrO concentration fixed at 2 pptv in the daytime marine boundary layer was run ("MBL BrO 2 pptv"). Increased BrO leads to increased OIO concentrations (BrO + IO → OIO + Br, R15), which leads to increased higher oxide production which in turn increases I_Y loss and decreases I_Y burden (10 %). The median bias in vertical comparisons with TORERO IO observations decreases by ∼ 12 to 71 %. Although the overall tropospheric O_3 burden decreases by 3.7 %, the average O_3 change at the surface is larger

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and shows a decrease of ∼ 8 % (Fig. 16) which is the largest decrease in O_3 found within these sensitivity simulations.

7.5 Ocean surface iodide (I^-) concentration

Chance et al. (2014) compiled the available ocean surface iodide (I^-) observations and investigated correlations with various environmental parameters. They found that ocean surface iodide correlated most strongly with the square of sea surface temperature, as used in this work. However MacDonald et al. (2014), using a sub-set of the Chance et al. (2014) data, found that an Arrhenius parameterisation gave best agreement. Figure 15 shows annual averaged ocean surface iodide generated from both parameterisations. The sea surface temperatures are taken from the annual mean GEOS field used in GEOS-Chem. The area weighted mean concentrations are 37.6 and 80.8 nM for MacDonald et al. (2014) and Chance et al. (2014), respectively. Both approaches reproduce the latitudinal gradient observed in Fig. 1 of Chance et al. (2014), however large discrepancies are apparent in magnitude. The dataset reported in Chance et al. (2014) has a median value of 77 nM and interquartile range of 28–140 nM.

Inclusion of the MacDonald et al. (2014) iodide parameterisation ("Ocean Iodide") reduces the inorganic iodine flux by 51 % to 1.9 Tg, which in turn decreases the global tropospheric iodine I_Y burden (23 %) and surface IO concentrations (34 %). The median bias in comparison with TORERO vertical profiles decreases by ∼ 47 to 42 %. Tropospheric O_3 burden increases by 2.1 % and global mean OH increase by 0.17 % with respect to the iodine simulation.

7.6 Higher oxide lifetime

Within the model we have considered the uptake of the I_2O_X ($X = 2,3,4$) to aerosol as an irreversible loss of iodine, with the same reactive probability (γ) as INO_2 (0.02).

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We assess our sensitivity to this assumption by running simulations doubling ("I_2O_X (γ) ×2") and halving this value ("I_2O_X (γ)/2").

The effect of doubling γ leads to decreasing global tropospheric I_Y burden (5.1 %), decreasing surface marine boundary layer (900 < hPa) IO (4.6 %), and decreases the median bias in vertical comparisons with TORERO IO (~ 6.9 %) to 75 %. This leads to a slightly increased global tropospheric O_3 burden (0.54 %), and marginally decrease in global mean OH (0.08 %). The effect of halving γ is essentially symmetrical, with an increased global tropospheric I_Y burden (4.3 %), increased surface marine boundary layer (900 < hPa) IO concentration (4.3 %), and an increased median bias in vertical comparisons with TORERO IO by ~ 4.4 to 84 %. This leads to slightly decreased global tropospheric O_3 burden (0.44 %), and marginally increase in OH (0.05 %).

7.7 Summary

Uncertainties in the atmospheric chemistry of iodine lead to some significant uncertainties on iodine's impact of atmospheric composition. Further laboratory studies on the photolytic properties of high oxides would reduce uncertainty, as would a more detailed understanding of the rates of heterogenous cycling on a range of aerosols. The interplay between bromine and iodine chemistry is also potentially significant for the oxidant budgets. Given the inorganic iodine emission's role as the largest source of iodine into the atmosphere, improved constraints on the concentration of oceanic iodide would also reduce uncertainties. It is clear that we do not have a complete understanding of iodine chemistry in the atmosphere and further laboratory and field observations are necessary to provide a stronger constraint.

8 Conclusions

We have implemented a representation of the tropospheric chemistry of iodine into the GEOS-Chem model and compared it against a range of observational datasets. We

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estimate a global emission of 3.8 Tg yr^{-1} of iodine, which is consistent with previous work. We find this dominated by the inorganic ocean source (84 %), and the majority (91 %) of deposition is back to the oceans.

Comparisons with the limited IO observational dataset shows that the model is within a factor of 2 of the observations on average. Iodine reduces the global tropospheric O_3 burden by ∼ 9 %. Global mean OH concentrations are increased (1.8 %) by the presence of iodine due to the reduction in the O_3-H_2O primary source being compensated for by an increased conversion of HO_2 into OH via the photolysis of HOI. Both changes involve HOI production and destruction cycles.

Our understanding of iodine chemistry is hampered by limited laboratory studies of both its gas and aerosol phase chemistry, by limited field measurements of atmospheric iodine compounds and poor understanding of ocean surface iodide and its chemistry. Impacts on O_3 and OH are sensitive to the uncertainty of ocean iodine emissions, the parameterisation of iodine recycling in aerosol, to the photolysis parameters for the higher oxides and to the assumed Br chemistry. Given its role as the largest component of atmospheric iodine, and its central role in both O_3 destruction and HO_2 to IO cycling, a priority should be given to instrumentation to measure HOI.

Appendix A:

A1 Additional details on sensitivity runs

A1.1 Details of reactions within scheme, but not present within IUPAC/JPL

The field of iodine chemistry is still young, and some reactions that are used within box model/global studies are not in the IUPAC/JPL compilations due to uncertainties in the laboratory studies or for other reasons. Differences choices have been made regarding reactions included in previous box model (Bloss et al., 2010; Mahajan et al., 2009; Read et al., 2008; Saiz-Lopez et al., 2008; Sommariva et al., 2012) and global

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model studies (Breider, 2010; Ordóñez et al., 2012; Saiz-Lopez et al., 2012b, 2014). The following reactions have been included within our simulation's chemistry scheme (Tables 3 and 4) although they are not in the IUPAC/JPL compilations.

M5 – $HOI + OH \rightarrow IO + H_2O$

Uncertainties exist over product channels for this reaction (Sommariva et al., 2012). In our study we assume the products are IO and H_2O based on laboratory experiments (Riffault et al., 2005) and previous box model analysis (Sommariva et al., 2012). It is not included within JPL/IUPAC compilations.

M12 – $INO_3 + I \rightarrow I_2 + NO_3$

This reaction's rate is based on a single theoretical study (Kaltsoyannis and Plane, 2008), and it is thus not included within either the JPL or IUPAC compilations. The impact of inclusion within a box model was found to be minimal, except in high iodine and NOx conditions (Sommariva et al., 2012). It is argued that this reaction rate needs determination with higher accuracy (Sommariva et al., 2012).

M17 – $OIO + OIO \rightarrow I_2O_4$

This reaction rate is from a single experimental study (Gómez Martín et al., 2007), which yielded a lower limit at $1.2 \pm 0.3 \times 10^{-10}$ cm^3 molec^{-1} s^{-1}. This reaction is not included within JPL/IUPAC compilations. This reaction is included in this work, along with the reverse reaction (Reaction T12, $I_2O_4 \rightarrow 2OIO$).

T7 – $IO + NO_2 \rightarrow INO_3$
T8 – $INO_3 \rightarrow IO + NO_2$

Good consensus exists between reaction rates (298 K) for the forward reaction (Reaction T7) from JPL (7.68×10^{-31} cm^3 molec^{-1} s^{-1}) and IUPAC ($7.96 \times$

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10^{-31} cm^3 $molec^{-1}$ s^{-1}). The reverse reaction (Reaction T8) is included in the IUPAC (Atkinson et al., 2007) without direct experiment observation. No recommendation is given in the recent recent JPL compilation (Sander et al., 2011). The INO_3 thermal stability used by studies has led to magnitude of differences between reaction rates (298 K) from 1.08×10^{-2} (Read et al., 2008) to 2.51×10^{-5} cm^3 $molec^{-1}$ s^{-1} (Sommariva et al., 2012). The latter uses the most recent theoretical study (Kaltsoyannis and Plane, 2008), which we also use here. The forward reaction (Reaction T7) has been included ubiquitously in iodine modelling work; and reverse reaction (Reaction T8) is employed in the majority of, but not all studies (Ordóñez et al., 2012). Both reactions are included in this work.

T9 – $IO + OIO \rightarrow I_2O_3$

A single experimental study (Gómez Martín et al., 2007) gives a upper and lower rate of 1.5×10^{-10} and 1.5×10^{-11} cm^3 $molec^{-1}$ s^{-1}, respectively. We use the higher value in this work as in others (Saiz-Lopez et al., 2008; Sommariva et al., 2012). The rate was found to increase with pressure over the range studied (10–400 hPa, Gómez Martín et al., 2007), suggesting greater importance at the higher pressures found at the surface.

T10 – $I_2O_2 + M \rightarrow IO + IO$

T11 – $I_2O_2 + M \rightarrow OIO + I$

These reaction has been studied solely theoretically (Kaltsoyannis and Plane, 2008) and are not included in JPL/IUPAC compilations. A temperature dependent rate was calculated theoretically using the Rice–Ramsperger–Kassel–Markus theory (Ordóñez et al., 2012) which is used in our work.

T12 – $I_2O_4 \rightarrow 2OIO$

The rate is calculated from the value for binding energy of the dimer (Kaltsoyannis and Plane, 2008), and is not included in JPL/IUPAC complications. Considering that we have included reaction M17 ($OIO + OIO \rightarrow I_2O_4$), we also include the reverse Reaction T12 in our work at the Kaltsoyannis and Plane (2008) rate.

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A1.2 Detail of reactive uptake coefficients (γ) used for heterogeneous reactions

As described in Sect. 3.1, we stoichiometrically emit I_2 following uptake of species that hydrolyse to HOI (INO_2, INO_3, HOI). We assume this to avoid double counting of Br_2 release already included within the model as described by Parrella et al. (2012). Lack of, or limited experimental data reduces certainty on heterogeneous processing of halogens. The reactive uptake coefficients (γ) used in this study are experimentally constrained wherever possible or follow previously estimated values in the literature as described below.

The JPL compilation notes a single experimental study of HOI uptake on H_2SO_4, yielding mass accommodation coefficients (α) in the range 0.02 to 0.07 (Sander et al., 2011). Another two studies on ice and salt are reported in JPL 10-6 with lower limits of > 0.0022 and > 0.01 respectively (Sander et al., 2011). IUPAC evaluates two experimental studies which "concur (the) uptake coefficient is large", but no recommendation is given due to possible uncertainties in reversibility (Crowley et al., 2010). The γ values used in literature range between 0.01 (Mahajan et al., 2009; Breider, 2010) and 0.5 (Saiz-Lopez et al., 2007). The higher end of this range originates from an investigation of the sensitivity to this a parameter within THAMO by Saiz-Lopez et al. (2007) for which the basecase was set as 0.02. A γ value of 0.02 is used within our work.

For INO_2 and INO_3 no experiment work is available on the uptake and values have previously been estimated by analogy with measured equivalent bromine species. For INO_3 a γ value of 0.01 has been frequently used based on estimations (Mahajan et al., 2009; Ordóñez et al., 2012), but values have been used up to 0.2 (Bloss et al., 2010). For INO_2 γ values of 0.01 (Mahajan et al., 2009) or 0.02 (Ordóñez et al., 2012; Saiz-Lopez et al., 2007) have often been used, but γ values up to 0.1 have also been used (Bloss et al., 2010). In this work γ values of 0.01 and 0.02 are used for INO_3 and INO_2 respectively.

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The IUPAC compilation includes a recommendation for HI uptake γ on ice of 0.2 (Crowley et al., 2010), based on three experimental studies. A γ value of 0.1 has most often been used in modelling studies (Breider, 2010; Mahajan et al., 2009; Saiz-Lopez et al., 2008) and is is used in this work.

For I_2O_X ($X = 2,3,4$) no experimental data is available for reactive uptake coefficients. The uptake has been discussed in the literature, including a box model study which tested sensitivity around a base value of 0.02 (Saiz-Lopez et al., 2008). The γ value for I_2O_X was set at 0.02 by with analogy INO_2. This value is highly uncertain and values up to 1 have been used for gamma in modelling studies (Bloss et al., 2010). A value of 0.02 is used within this work.

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Table 1. Total simulated emissions for iodinated species. Values are given as annual totals in Tg of iodine.

Species	Emissions Tg I yr^{-1}
CH_3I	0.26
CH_2I_2	0.11
CH_2ICl	0.18
CH_2IBr	0.05
I_2	0.32
HOI	2.91
Total	3.83

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Table 2. Henry's law coefficients and molar heats of formation of iodine species. Where Henry's law constant equals infinity a very large values is used within the model (1×10^{20}). For I_2O_X ($X = 2,3,4$) a Henry's law constant of infinity is assumed by analogy with INO_3.

Num.	Species	Henry's Law Constant $M\,atm^{-1}$	Reference	Molar Heat of Formation $298\,K/R$ (K)	Reference
D1	HOI	1.53×10^4	Sander (1999)	-8.37×10^3	Sander et al. (2006)
D2	HI	2.50×10^1	Sander (1999)	-3.19×10^3	Sander et al. (2006)
D3	INO_3	∞	Vogt et al. (1999)	-3.98×10^4	Kaltsoyannis and Plane (2008)
D4	I_2O_2	∞	see caption text	-1.89×10^4	Kaltsoyannis and Plane (2008)
D5	I_2	2.63×10^0	Sander (1999)	-7.51×10^3	Sander et al. (2006)
D6	INO_2	3.00×10^{-1}	Vogt et al. (1999)	-7.24×10^3	Sander et al. (2006)
D7	I_2O_3	∞	see caption text	-7.70×10^3	Kaltsoyannis and Plane (2008)
D8	I_2O_4	∞	see caption text	-1.34×10^4	Kaltsoyannis and Plane (2008)

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Table 3. Bimolecular iodine reactions. These are given in the Arrhenius form with the rate equal to $A \cdot \exp(\frac{Ea}{RT})$. Unknown values are represented by a dash and these set to zero in the model, reducing the exponent to 1.

Rxn ID	Reaction	A $cm^3\,molec^{-1}\,s^{-1}$	Ea/R K	Citation
M1	$I + O_3 \rightarrow IO + O_2$	2.10×10^{-11}	−830	Atkinson et al. (2007)
M2	$I + HO_2 \rightarrow HI + O_2$	1.50×10^{-11}	−1090	Sander et al. (2011)
M3	$I_2 + OH \rightarrow HOI + I$	2.10×10^{-10}	–	Atkinson et al. (2007)
M4	$HI + OH \rightarrow I + H_2O$	1.60×10^{-11}	440	Atkinson et al. (2007)
M5	$HOI + OH \rightarrow IO + H_2O$	5.00×10^{-12}	–	Riffault et al. (2005)
M6	$IO + HO_2 \rightarrow HOI + O_2$	1.40×10^{-11}	540	Atkinson et al. (2007)
M7	$IO + NO \rightarrow I + NO_2$	7.15×10^{-12}	300	Atkinson et al. (2007)
M8	$HO + CH_3I \rightarrow H_2O + I\,(CH_2I)$	4.30×10^{-12}	−1120	Atkinson et al. (2008)
M9	$INO + INO \rightarrow I_2 + 2NO$	8.40×10^{-11}	−2620	Atkinson et al. (2007)
M10	$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	4.70×10^{-12}	−1670	Atkinson et al. (2007)
M11	$I_2 + NO_3 \rightarrow I + INO_3$	1.50×10^{-12}	–	Atkinson et al. (2007)
M12	$INO_3 + I \rightarrow I_2 + NO_3$	9.10×10^{-11}	−146	Kaltsoyannis and Plane (2008)
M13	$I + BrO \rightarrow IO + Br$	1.20×10^{-11}	–	Sander et al. (2011)
M14	$IO + Br \rightarrow I + BrO$	2.70×10^{-11}	–	Bedjanian et al. (1997)
M15	$IO + BrO \rightarrow Br + I + O_2$	3.00×10^{-12}	510	Atkinson et al. (2007)
M16	$IO + BrO \rightarrow Br + OIO$	1.20×10^{-11}	510	Atkinson et al. (2007)
M17	$OIO + OIO \rightarrow I_2O_4$	1.50×10^{-10}	–	Gómez Martín et al. (2007)
M18	$OIO + NO \rightarrow NO_2 + IO$	1.10×10^{-12}	542	Atkinson et al. (2007)

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Table 4. Termolecular iodine reactions. The lower pressure limit rate (k_0) is given by: $A_0 \cdot \exp(\frac{Ea_0}{RT}) \cdot (\frac{300}{T})^x$. The high pressure limit rate k($_\infty$) is given by: $A_\infty \cdot \exp(\frac{Ea_\infty}{RT})$. Fc characterises the fall off curve of the reaction as described by Atkinson et al. (2007). Unknown values are represented by a dash and these set to zero in the model, reducing the exponent to 1. Reverse equilibrium reaction rates (Keq) for T3* and T5* are from from Atkinson et al. (2007) given as $1.0 \times 10^{-6} \exp(9160/T)$ and $1.0 \times 10^{-6} \exp(9200/T)$ respectively.

Rxn ID	Reaction	A_0 $cm^3\,molec^{-1}\,s^{-1}$	Ea_0/R K	x	A_∞ $cm^3\,molec^{-1}\,s^{-1}$	Ea_∞/R K	Fc	Citation
T1	$IO + IO + O_2 \rightarrow I + OIO$	2.16×10^{-11}	180	–	–	–	–	Atkinson et al. (2007)
T2	$IO + IO + O_2 \rightarrow I_2O_2$	3.24×10^{-11}	180	–	–	–	–	Atkinson et al. (2007)
T3*	$I + NO + M \rightleftharpoons INO$	1.80×10^{-32}	300	1	1.70×10^{-11}	9200	0.60	Atkinson et al. (2007)
T4	$INO \rightarrow I + NO$	2.00×10^{-5}	–	–	–	–	–	Atkinson et al. (2007)
T5*	$I + NO_2 + M \rightleftharpoons INO_2$	3.00×10^{-31}	300	1	6.60×10^{-11}	96000	0.63	Atkinson et al. (2007)
T6	$INO_2 \rightarrow I + NO_2$	3.72×10^{-7}	–	–	–	–	–	Atkinson et al. (2007)
T7	$IO + NO_2 \rightarrow INO_3$	7.70×10^{-31}	–	5	1.60×10^{-11}	–	0.40	Atkinson et al. (2007)
T8	$INO_3 + M \rightarrow IO + NO_2$	2.10×10^{15}	−13670	–	–	–	0.60	Kaltsoyannis and Plane (2008)
T9	$IO + OIO + M \rightarrow I_2O_3$	1.50×10^{-10}	–	–	–	–	–	Gómez Martín et al. (2007)
T10	$I_2O_2 + M \rightarrow IO + IO$	1.00×10^{12}	−9770	–	–	–	0.60	Ordóñez et al. (2012)
T11	$I_2O_2 + M \rightarrow OIO + I$	2.50×10^{14}	−9770	–	–	–	0.60	Ordóñez et al. (2012)
T12	$I_2O_4 + M \rightarrow 2OIO$	3.80×10^{-2}	–	–	–	–	–	Kaltsoyannis and Plane (2008)

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Table 5. Photolysis reactions of iodine species. For I_2O_X ($X = 2,3,4$) the cross-section of INO_3 is used as described in Sect. 2.4.

ID	Reaction	Reference cross-section
J1	$I_2 + h\nu \rightarrow 2I$	Sander et al. (2011)
J2	$HOI + h\nu \rightarrow I + OH$	Sander et al. (2011)
J3	$IO + h\nu \rightarrow I + [O_3]$	Sander et al. (2011)
J4	$OIO + h\nu \rightarrow I + O_2$	Sander et al. (2011)
J5	$INO + h\nu \rightarrow I + NO$	Sander et al. (2011)
J6	$INO_2 + h\nu \rightarrow I + NO_2$	Sander et al. (2011)
J7	$INO_3 + h\nu \rightarrow I + NO_3$	Sander et al. (2011)
J8	$I_2O_2 + h\nu \rightarrow I + OIO$	see Sect. 2.4
J9	$CH_3I + h\nu \rightarrow I + CH_2O_2$	Sander et al. (2011)
J10	$CH_2I_2 + h\nu \rightarrow 2I + (CH_2)$	Sander et al. (2011)
J11	$CH_2ICl + h\nu \rightarrow I + (CH_2Cl)$	Sander et al. (2011)
J12	$CH_2IBr + h\nu \rightarrow I + (CH_2Br)$	Sander et al. (2011)
J20	$I_2O_4 + h\nu \rightarrow 2OIO$	see Sect. 2.4
J21	$I_2O_3 + h\nu \rightarrow OIO + IO$	see Sect. 2.4.

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Table 6. Heterogeneous reactions of iodine species. Where measured values have not been reported estimated values are used and no reference is given, further detail on uptake choices is in Sect. A1.2. Stared (*) reactions proceed only on sea-salt aerosols.

ID	Reaction	Reactive uptake coefficient (γ)	Reference
K1	HI $\rightarrow$ iodine aerosol	0.10*	Crowley et al. (2010)
K2	$INO_3 \rightarrow 0.5I_2$	0.01*	see caption text
K3	HOI $\rightarrow 0.5I_2$	0.01*	Sander et al. (2011)
K4	$INO_2 \rightarrow 0.5I_2$	0.02*	see caption text
K5	$I_2O_2 \rightarrow$ iodine aerosol	0.02	see caption text
K6	$I_2O_4 \rightarrow$ iodine aerosol	0.02	see caption text
K7	$I_2O_3 \rightarrow$ iodine aerosol	0.02	see caption text

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Table 7. Comparison between global tropospheric O_X budgets of standard GEOS-Chem (v9-2) which includes bromine chemistry and the iodine simulation described here which includes both iodine and bromine chemistry. Recent average model values from Young et al. (2013) are also shown. For the IO + BrO halogen crossover reaction we allocate half the O_3 loss to bromine and half to iodine. Values are rounded to the nearest integer value.

Scenario	GEOS-Chem simulation (v9-2)	Iodine simulation	ACCENT Young et al. (2013)
O_3 burden (Tg)	367	334	340 ± 40
O_X chemical Sources (Tg Yr^{-1})			
NO + HO_2	3512	3529	–
NO + CH_3O_2	1269	1307	–
Other O_X sources	505	521	–
Total chemical O_X sources (PO_X)	5286	5357	5110 ± 606
O_X chemical sinks (Tg Yr^{-1})			
$O_3 + h\nu + H_2O \rightarrow 2OH$	2425	2119	–
$O_3 + HO_2 \rightarrow OH + O_2$	1274	1080	–
$O_3 + OH \rightarrow HO_2 + O_2$	621	560	–
$HOBr + h\nu \rightarrow Br + OH$	166	143	–
$HOBr + HBr \rightarrow Br_2 + H_2O$ (aq. aerosol)	8	8	–
$BrO + BrO \rightarrow 2Br + O_2$	12	10	–
$BrO + BrO \rightarrow Br_2 + O_2$	3	3	–
$BrO + OH \rightarrow Br + HO_2$	6	5	–
$IO + BrO \rightarrow Br + I + O_2$	–	7	–
Other bromine O_X sinks	1	1	–
Total bromine O_X sinks	195	178	–
$HOI + h\nu \rightarrow I + OH$	–	583	–
$HOI \rightarrow 0.5I_2$ (seasalt aerosol)	–	2	–
$IO + BrO \rightarrow Br + I + O_2$	–	7	–
$OIO + h\nu \rightarrow I + O_2$	–	156	–
Other iodine O_X sinks	–	1	–
Total iodine O_X sinks	–	748	–
Other O_X sinks	172	173	–
Total chem. O_X sinks (LO_X)	4687	4864	4668 ± 727
O_3 $P(O_X)$-$L(O_X)$ (Tg Yr^{-1})	599	493	442 (aprox.)
O_3 Dry deposition (Tg Yr^{-1})	886	791	1003 ± 200
O_3 Lifetime (days)	24	22	22 ± 2
O_3 STE (PO_X-LO_X-Dry dep.) (Tg Yr^{-1})	287	298	552 ± 168

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Table A1. Effects of sensitivity runs on relevant variables. Values are shown as percentage change from the iodine simulation in the troposphere as global means unless otherwise stated. MBL = Marine Boundary Layer (900 < hPa), O_X is defined as in the text. CH_4 lifetime is calculated globally in the troposphere with respect to loss by reaction with OH.

	Mean IO MBL surface concentration	Chem. O_X loss (LO_X)	Chem. O_X prod. (PO_X)	PO_X -LO_X	O_3 burden	O_3 deposition
Just org. I	−83.45	−1.64	−3.11	17.69	5.53	7.19
I_2O_X loss (γ) ×2	−4.26	−0.15	−0.28	1.61	0.54	0.59
I_2O_X loss (γ)/2	3.93	0.13	0.24	−1.34	−0.44	−0.52
Het. cycle (γ) ×2	2.21	0.04	0.16	−1.61	−0.69	−0.56
Het. cycle (γ)/2	−1.84	−0.06	−0.14	1.07	0.56	0.45
No Het. cycle	−48.03	−1.15	−2.20	12.60	4.09	5.23
Sulphate Uptake	−22.49	−1.25	−2.26	12.06	4.54	4.94
Ocean iodide	−34.28	−0.66	−1.26	7.24	2.06	3.01
I_2O_X X-sections ×2	4.30	0.11	0.22	−1.34	−0.40	−0.47
I_2O_X exp. X-sections	6.73	0.19	0.35	−1.88	−0.60	−0.73
No I_2O_X Photolysis	−39.35	−1.10	−2.12	12.33	5.05	4.86
MBL BrO 2 pptv	−6.78	−3.59	−2.71	−15.28	−3.73	−6.03

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Table A1. Continued.

	OH mean concentration	HO_2 mean concentration	HO_2 /OH	I_Y lifetime	IO_X lifetime	I_Y burden	CH_4 lifetime
Just org. I	−0.64	3.53	4.19	123.92	16.09	−64.26	0.21
I_2O_X loss (γ) ×2	−0.08	0.27	0.36	−8.38	−0.93	−5.08	0.03
I_2O_X loss (γ)/2	0.05	−0.22	−0.27	8.00	0.55	4.27	−0.01
Het. cycle (γ) ×2	0.09	−0.39	−0.49	4.61	1.13	5.98	0.00
Het. cycle (γ)/2	−0.09	0.32	0.41	−3.89	−0.96	−5.04	0.02
No Het. cycle	−0.47	2.58	3.07	−61.18	5.38	−46.69	0.15
Sulphate Uptake	−0.87	2.70	3.60	−59.60	0.49	−48.49	0.52
Ocean iodide	−0.17	1.22	1.39	16.90	2.77	−23.42	0.01
I_2O_X X-sections ×2	0.05	−0.20	−0.25	5.26	0.61	3.10	−0.01
I_2O_X exp. X-sections	0.08	−0.31	−0.39	8.31	0.84	4.81	−0.01
No I_2O_X Photolysis	−0.90	2.54	3.48	−46.41	−17.68	−34.58	0.32
MBL BrO 2 pptv	−3.31	−1.44	1.93	−3.72	3.33	−10.07	4.17

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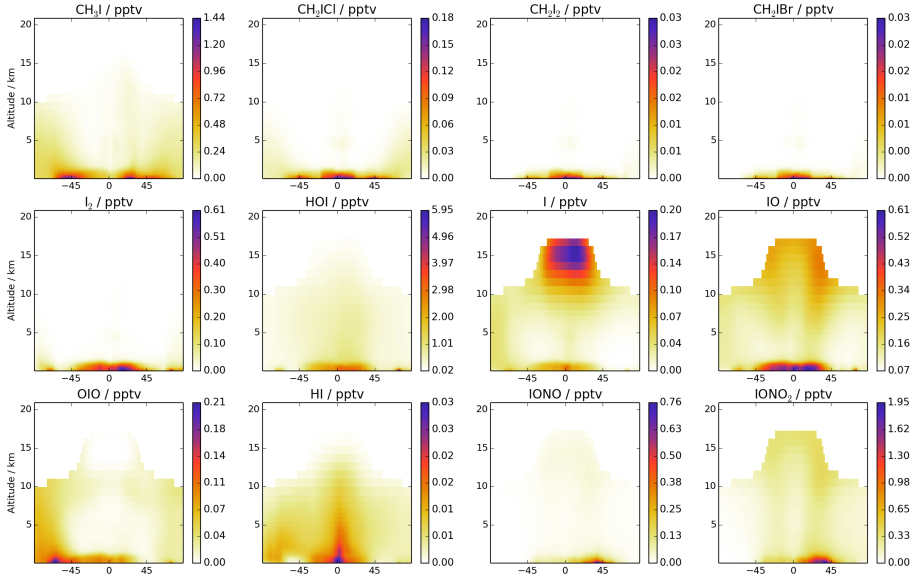

Figure 1. Annual mean zonal tropospheric mixing ratios for precursor and reactive iodine compounds (pptv). No calculations of concentrations are made within the stratosphere and so that region is left blank.

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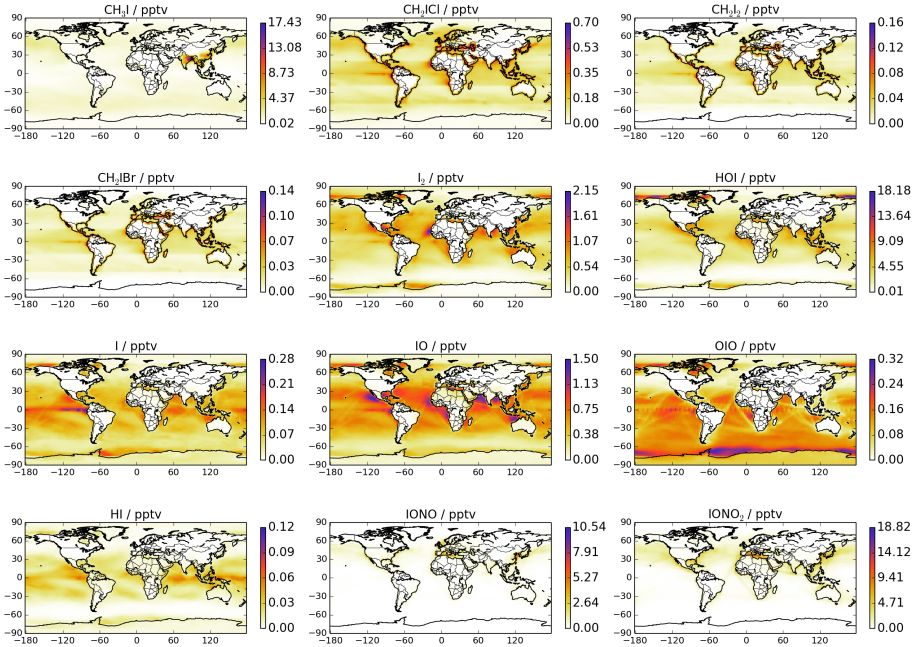

Figure 2. Annual mean surface mixing ratios for precursor and reactive iodine (pptv).

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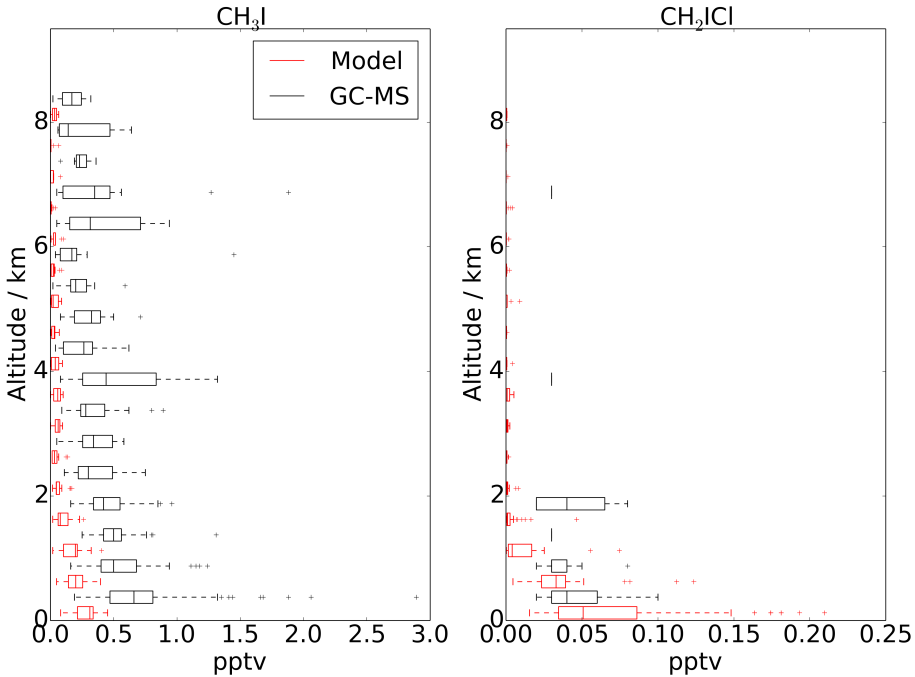

Figure 3. Vertical comparison of observations from the CAST (Combined Airborne Studies in the Tropics) campaign in the mid Pacific (Guam). The observations are shown in black and modelled values in red. The observations are from the FAAM BAE-146 research aircraft Whole Air Samples (WAS) analysed by Gas Chromatography-Mass Spectrometry (GC-MS). The box-plot extents give the inter-quartile range, with the median shown within the box. The whiskers give the most extreme point within 1.5 times the inter-quartile range.

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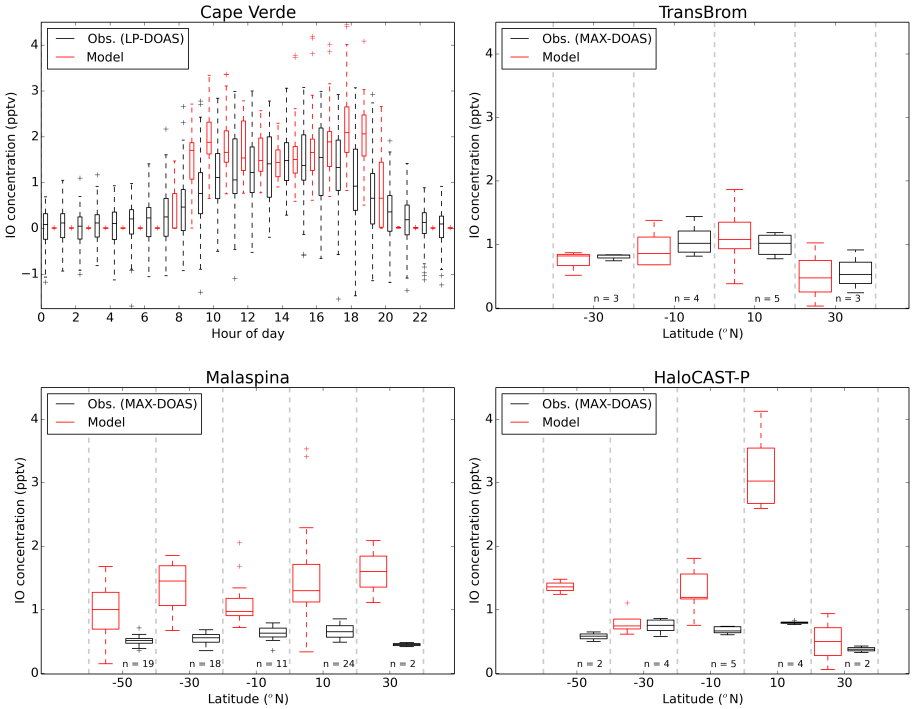

Figure 4. Iodine oxide (IO) surface observations (red) by campaign compared against model (black). Cape Verde measurements are shown against hour of day and others are shown as a function of latitude. Observations are from Cape Verde (Tropical Atlantic Mahajan et al., 2010; Read et al., 2008), Transbrom (West Pacific, Großmann et al., 2013), the Malaspina circumnavigation (Prados-Roman et al., 2015b), and HaloCAST-P (East Pacific, Mahajan et al., 2012). Number of data points within latitudinal bin are shown as "n". The boxplot extents give the inter-quartile range, with the median shown within the box. The whiskers give the most extreme point within 1.5 times the inter-quartile range.

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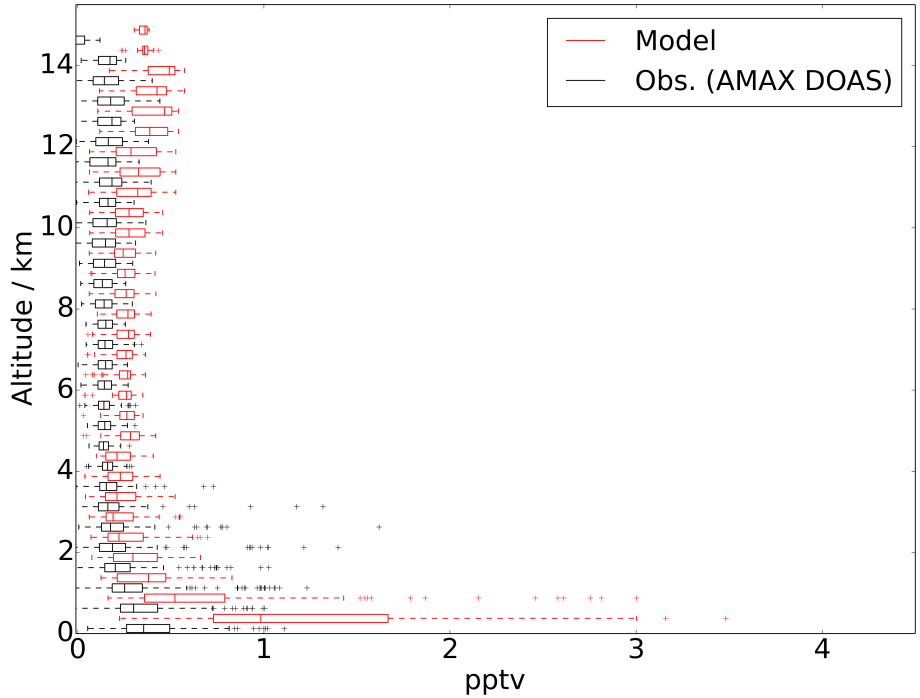

Figure 5. Vertical comparison of modelled and measured iodine oxide (IO) during the TORERO research campaign. Model and observations are in red and black respectively. Measurements were taken aboard the NSF/NCAR GV research aircraft by the University of Colorado airborne Multi-Axis DOAS instrument (CU AMAX-DOAS) as part of the TORERO campaign (Volkamer et al., 2015; Wang et al., 2015) in the eastern Pacific in January and February 2012. The boxplot extents give the inter-quartile range, with the median shown within the box. The whiskers give the most extreme point within 1.5 times the inter-quartile range.

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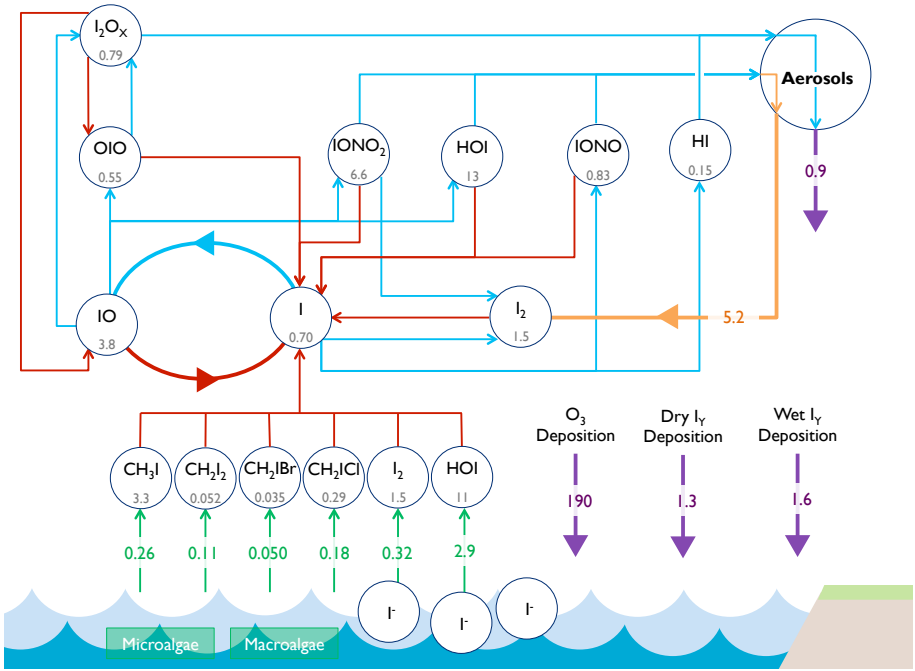

Figure 6. Schematic representation of implemented iodine chemistry. Average global annual mean burdens (Gg I) are shown below key I_Y species, with fluxes ($Tg\,I\,yr^{-1}$) shown on arrows. Red lines = photolysis, blue = chemical pathways, green lines = emission source, orange lines = heterogeneous pathway. This equates to a total iodine source and sink of $3.8\,Tg\,I\,yr^{-1}$. O_3 deposition in Tg is also shown to illustrate the driving force behind the inorganic emissions.

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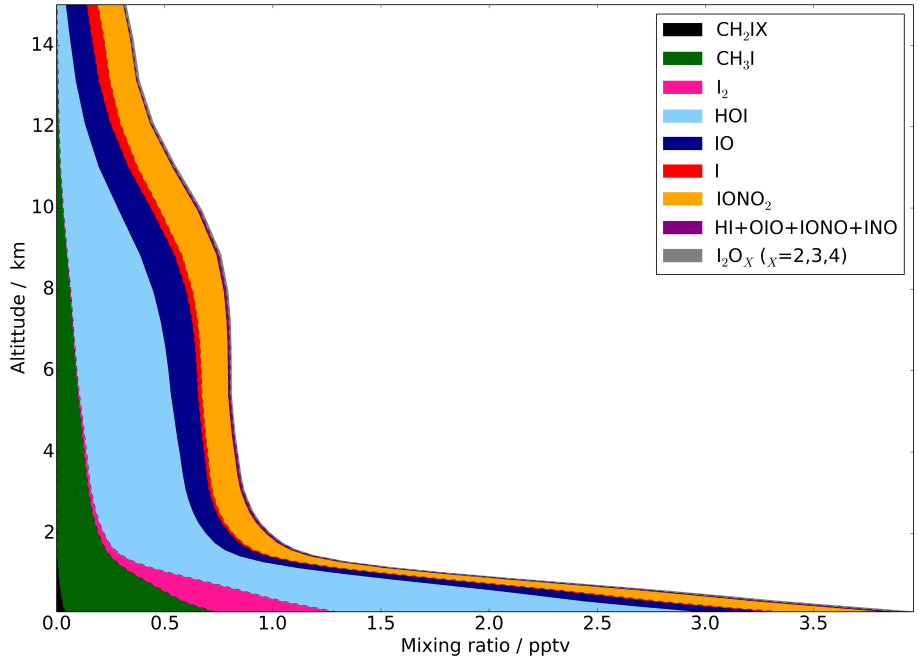

Figure 7. Global annual mean gas-phase iodine speciation with altitude. Mixing ratios are shown in pptv, with higher iodine oxides (I_2O_X ($X = 2,3,4$)) and di-halogenated organics (CH_2IX (X = Cl, Br, I)) grouped.

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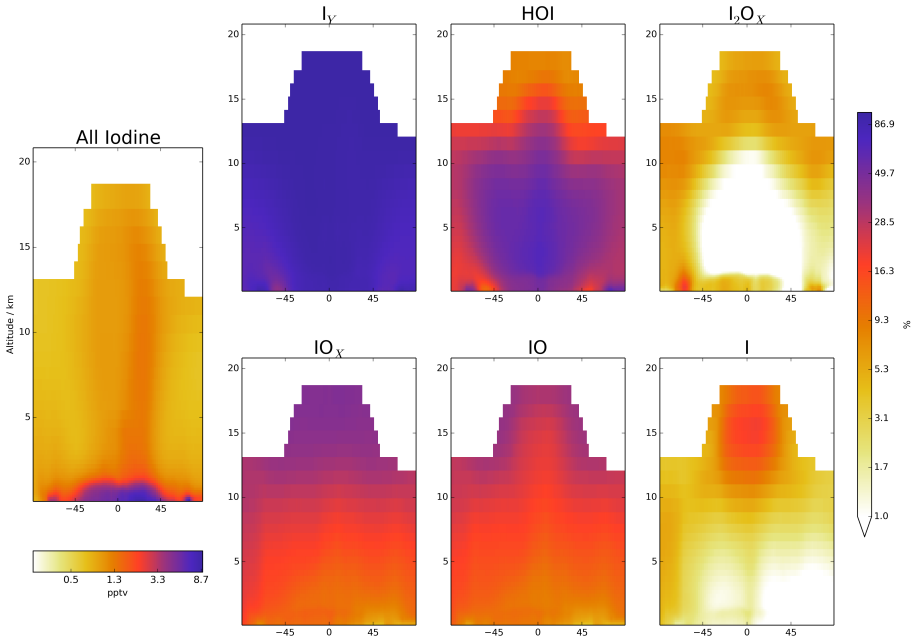

Figure 8. Zonal breakdown of global annual mean iodine speciation by family. First panel shows total gas phase iodine concentration and the following panels show percentage of different compounds to this. Total gas phase iodine = $CH_3I + 2CH_2I_2 + CH_2IBr + CH_2ICl + 2I_2 + HOI + IO + OIO + HI + INO_2 + INO_3 + 2I_2O_2 + 2I_2O_3 + 2I_2O_4 + I + INO$; $I_Y = 2I_2 + HOI + IO + OIO + HI + INO + INO_2 + INO_3 + 2I_2O_2 + 2I_2O_3 + 2I_2O_4$; $IO_X = I + IO$.

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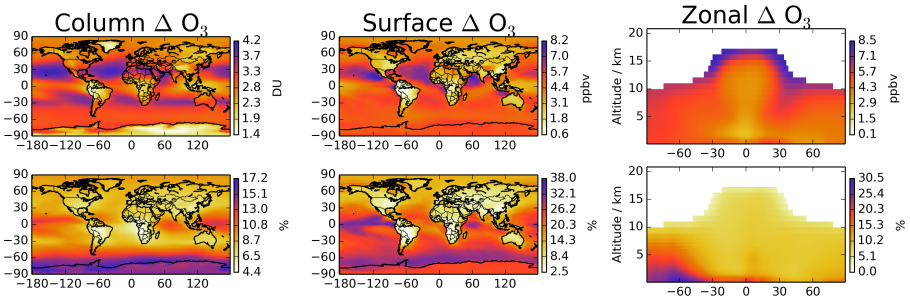

Figure 9. Decreases in annual mean tropospheric column, surface and zonal O_3 with inclusion of iodine chemistry are shown on left, middle and right panels respectively. Upper panels show changes in Dobson units or ppbv and lower panels show changes in percentage terms. This is calculated as the difference in the O_3 concentrations between standard GEOS-Chem (v9-2, including bromine) and the iodine simulation.

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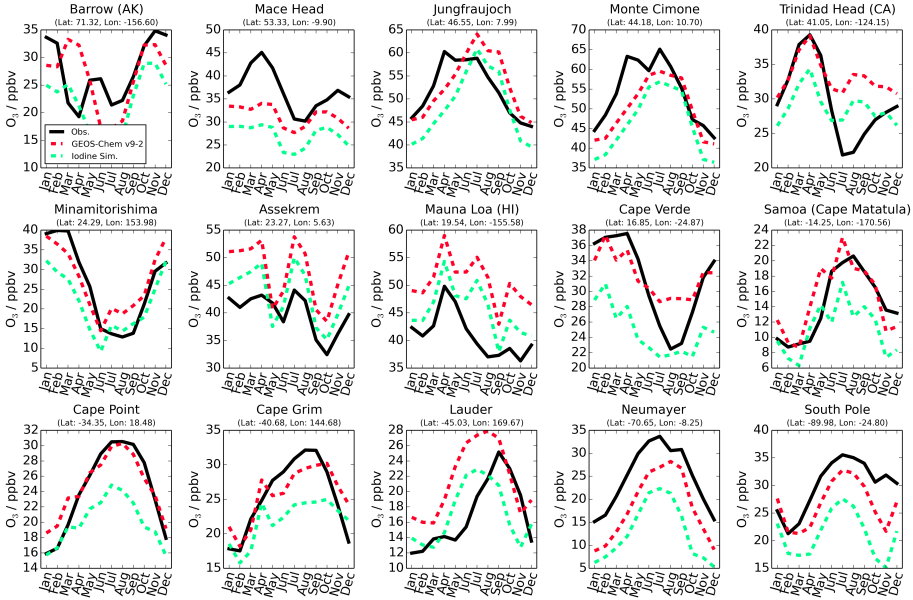

Figure 10. Seasonal cycle of near-surface O_3 at a range of Global Atmospheric Watch (GAW) sites (Sofen et al., 2015). Observational data shown is a 6 year monthly average (2006–2012). Model data is for 2005. Data is from GAW compile and processed as described in (Sofen et al., 2015). Red indicates standard GEOS-Chem (v9-2, including bromine) and green with inclusion of iodine chemistry.

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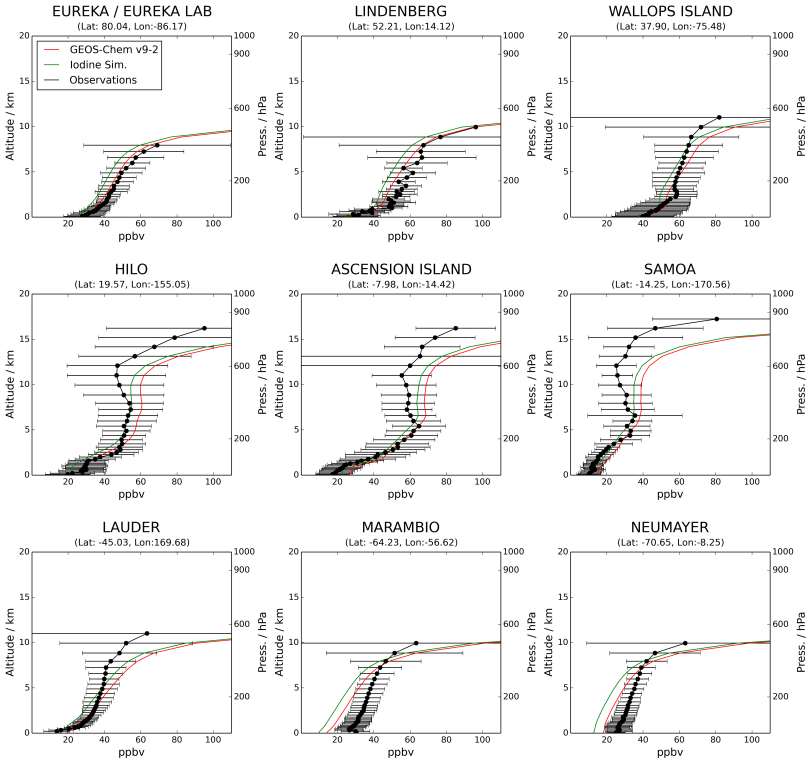

Figure 11. Comparison between annual modelled O_3 profiles and sonde data (2005,WOUDC, 2014). Profiles shown are the annual mean of available observations from World Ozone and Ultraviolet Radiation Data Centre WOUDC (2014) and model data for 2005 at given locations. The standard GEOS-Chem (v9-2) and the iodine simulation are shown in red and green respectively. Observations (in black) show mean concentrations with upper and lower quartiles given by whiskers.

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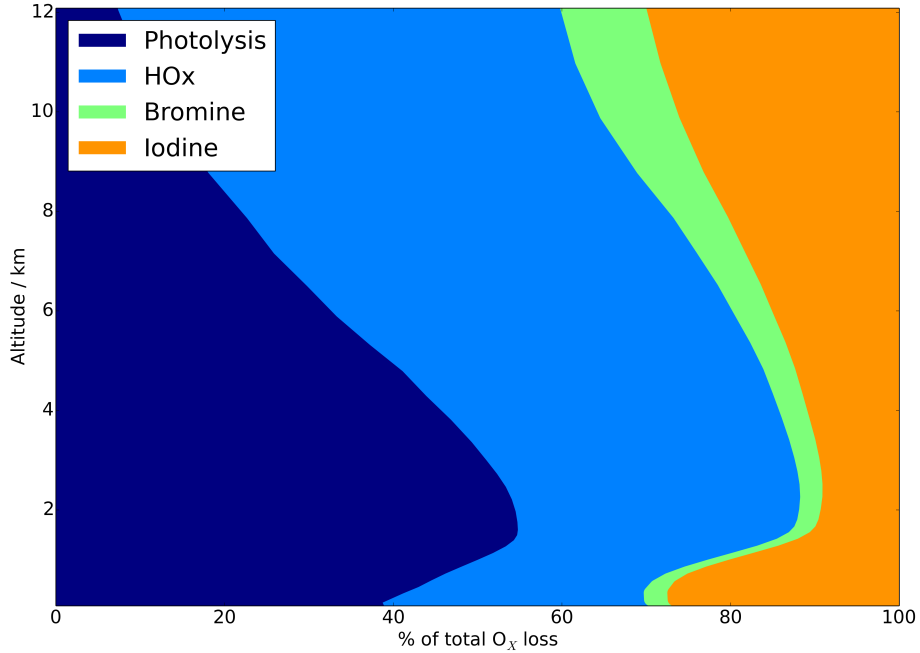

Figure 12. Vertical profile of simulated fractional global annual mean O_X loss by route. O_X definition is given in text. Photolysis represents loss of O_X due to O_3 photolysis in the presence of water vapour. HO_X loss includes routes via minor NO_X channels. The magnitude of the bromine route is probably underestimated as discussed in Sect. 2.6.

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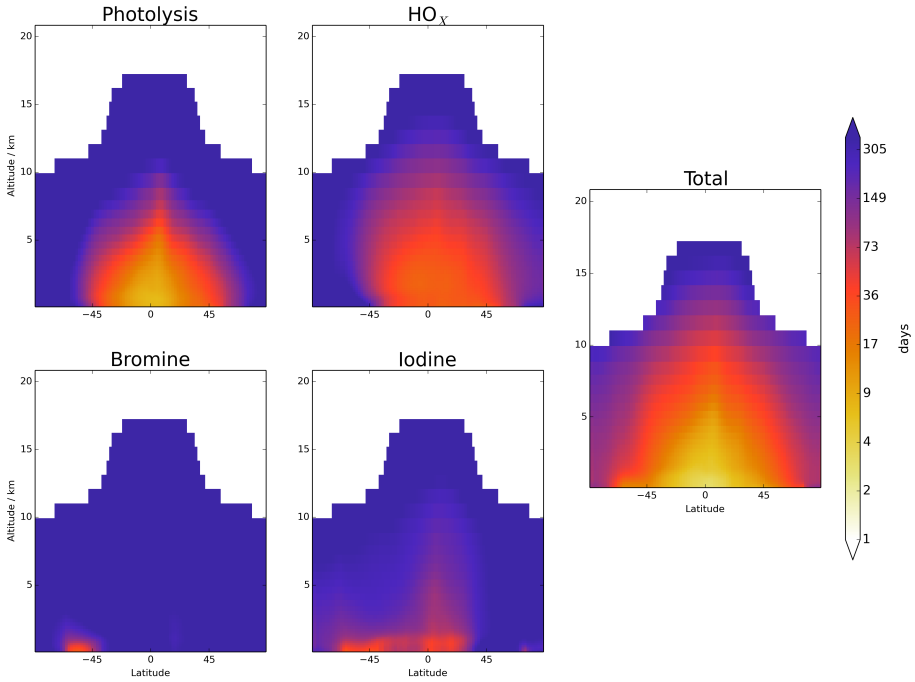

Figure 13. Global annual O_3 mean zonal chemical lifetime for different O_X loss routes (Photolysis, HO_X, Iodine, Bromine, and Total). Values are shown on a log on a scale.

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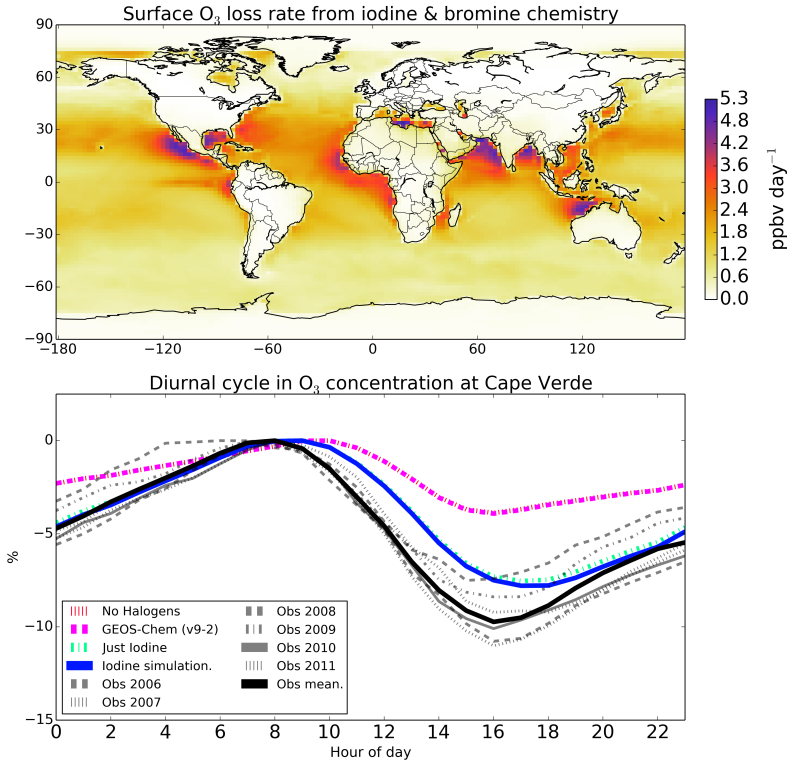

Figure 14. Global annual mean surface O_3 loss (ppbv day^{-1}) from both bromine and iodine compared to a simulation with neither (top), comparison between modelled and observed fractional diurnal O_3 cycles at the Cape Verde Observatory for 4 simulations (bottom). The diurnal change is calculated by subtracting each day's maximum O_3 concentration from the observations (2006–2012), then dividing by the daily means to give a diurnal fraction. Diurnal changes are averaged over the whole dataset. Lines are black, red, turquoise, green and magenta for mean of observations, "no hal", standard GEOS-Chem (v9-2), "just iodine" and iodine simulation respectively. Individual years of observational data are shown in grey.

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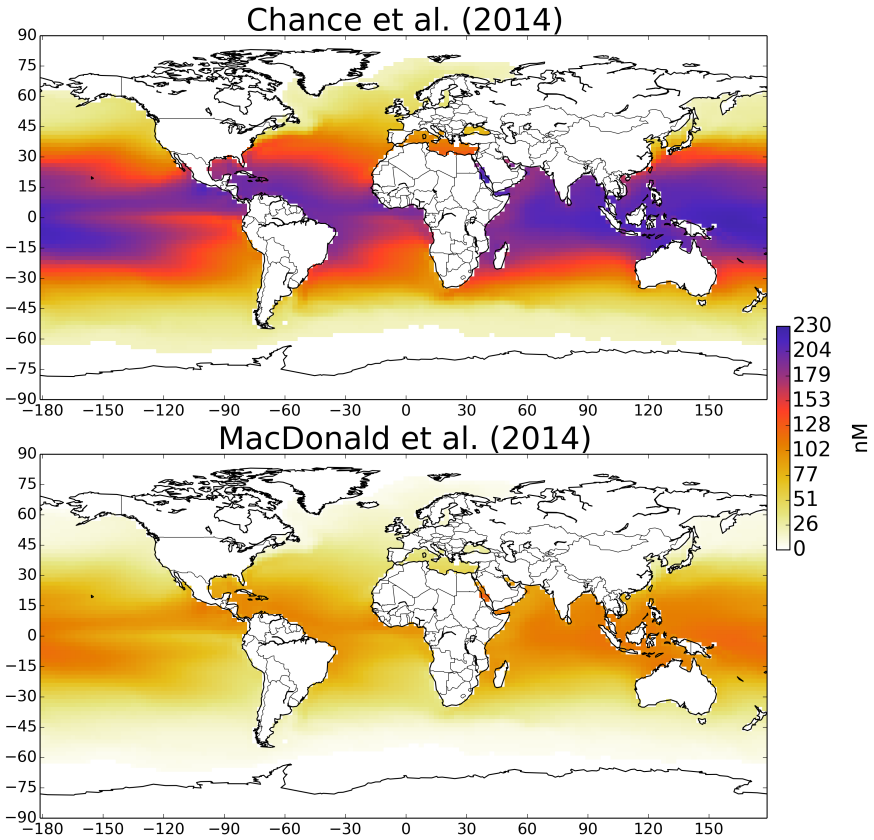

Figure 15. Calculated annual mean ocean surface iodide concentrations (I^-) in nM. Values are calculated from the highest correlation relationship (square) presented in Chance et al. (2014) Table 2 (top) and from Arrhenius relationship from Eq. (1) in MacDonald et al. (2014) (bottom). The Chance et al. (2014) parameterisation is used as the standard in the work with the MacDonald et al. (2014) used as the "Ocean iodide" sensitivity simulation in Sect. 7.

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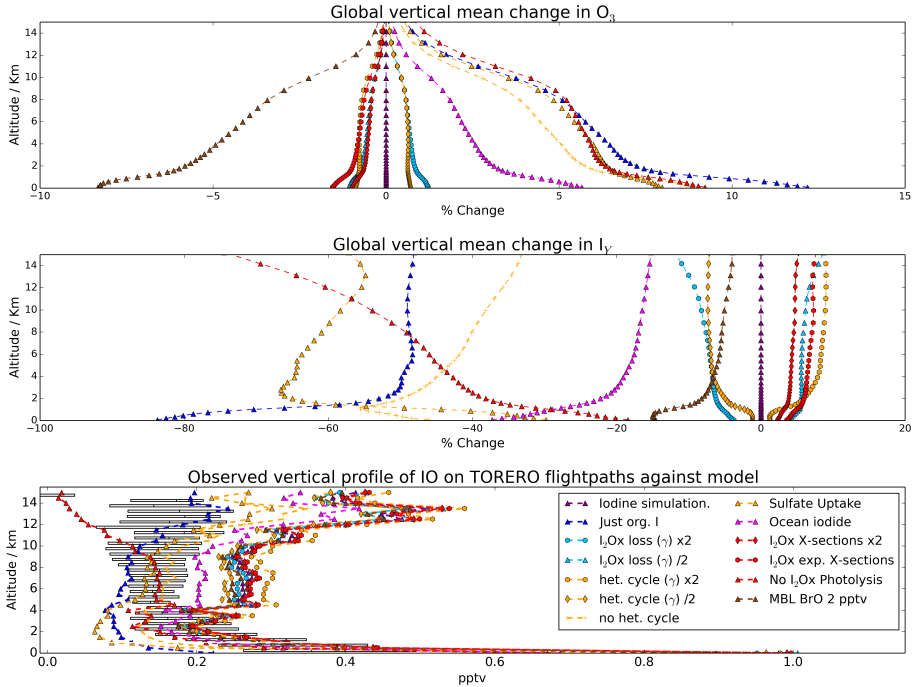

Figure 16. Sensitivity impacts. Upper and middle panels show global mean vertical percentage changes in concentrations of O_3, and I_Y. Lower panel gives vertically averaged iodine oxide (IO) mixing ratios (pptv) calculated along the TORERO Volkamer et al. (2015); Wang et al. (2015) flightpaths. The legend (bottom) is shared by all plots. The boxplot of IO observations (black) represents the quartiles of the data, with the median shown within the box.

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