Manuscript prepared for Atmos. Chem. Phys. Discuss. with version 2015/04/24 7.83 Copernicus papers of the LATEX class copernicus.cls. Date: 12 January 2016

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 re-5 cent iodine oxide (IO) observations, the simulation shows an average bias of $\sim +90$ % with available surface observations in the marine boundary layer (outside of polar regions), and of $\sim +73$ % within the free troposphere (350 hPa < p < 900 hPa) over the eastern Pacific. lodine emissions (3.8 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 10 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 (see Footnote 1) $(748 \text{ Tg O}_{x} \text{ yr}^{-1})$ due to photolysis of HOI (78 %), photolysis of OIO (21 %), and reaction between IO and BrO (1%). Increases in global mean OH concentrations (1.8%) by increased 15 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 io-20 dine driven tropospheric O₃ burden decrease of 14.4% compared to a simulation without iodine and bromine chemistry in the model, and a small increase in OH (1.8%). This is a significant impact and so halogen chemistry needs to be considered in both climate and air quality models.

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¹Here O_X is defined as $O_3 + NO_2 + 2NO_3 + PAN + PMN + PPN + HNO_4 + 3N_2O_5 + HNO_3 + BrO + HO$ where PAN = peroxyacetyl nitrate, PPN = peroxypropionyl nitrate, MPN = methyl peroxy nitrate, andMPN = peroxymethacryloyl nitrate.

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Introduction 1

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 5 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 basic chemistry of O_3 and OH in the troposphere is coupled and the central aspects 10 of this are well known (Young et al., 2013). Over the last decades significant research effort has gone into understanding the production of O₃, 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 focussed on its chemical destruction. O_3 is chemically
- lost in the troposphere predominantly through photolysis in the presence of water or its 15 reactions with HO₂ and OH (Lelieveld and Dentener, 2000). However, 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 iodine has arguably the more complex chemistry.
- Historically the dominant source of iodine was thought to be iodinated organic com-20 pounds from the ocean (Chuck et al., 2005; Jones et al., 2010; Law and Sturges, 2006). More recently, emission of inorganic halogen compounds (I₂ and HOI) has been identified as a significant source (Carpenter et al., 2013). Our understanding of its chemistry has been described in recent publications (Saiz-Lopez et al., 2012b; Sommariva et al., 2012).
- Once emitted into the atmosphere, the highly labile iodinated precursors rapidly photolyse 25 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 $(+HO_2, +IO_1, +NO_2, +BrO)$ 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.

Much of the uncertainty in iodine chemistry involves the production and fate of their higher oxides (I_2O_X) . These higher oxides are formed from a chain reaction of IO self reactions. (Sommariva et al., 2012).

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$O_3 + I \rightarrow IO + O_2$	(R1)
$IO + IO \rightarrow OIO + I$	(R2)
$\rm IO + \rm IO \rightarrow \rm I_2O_2$	(R3)
$\rm IO + OIO \rightarrow I_2O_3$	(R4)
$OIO + OIO \rightarrow I_2O_4$	(R5)

Due to their short lifetimes and low 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 = CI, Br, I) and inorganic (e.g. IO, OIO, I₂) species (Saiz-Lopez et al., 2012b).

Recent 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) have enabled the development of global organic halogen emissions (Ordóñez et al., 2012; Ziska et al., 2013) and more recently, datasets of IO observations with extensive geographical coverage (Prados-Roman et al., 2015b; Volkamer et al., 2015; Wang et al., 2015).

lodine 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.

When considered alongside bromine chemistry, box model studies have shown the magnitude of halogen driven O_3 loss processes to be up to 45% (Mahajan et al., 2009; Read

- $_{5}$ et al., 2008) of the total loss. Iodine can change the local HO₂ : OH ratio due to the production of HOI from HO₂ and IO, and its subsequent photolysis to release OH (Bloss, 2005; Chameides and Davis, 1980). Perturbation to the NO : NO₂ 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 NO₂, which affects O₃ 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 demonstrated that these O₃ loss processes also occur in remote non-coastal locations.
- 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). Inclusion of tropospheric bromine, iodine and chlorine chemistry into a global model led to significant changes in the composition troposphere. Tropospheric marine average O₃ columns decrease on the order of ~ 10 % (Saiz-Lopez et al., 2012a, 2014). As in the box model studies, up to ~ 30 % of the O₃ loss in the marine boundary layer (900 hPa <p) is found to be driven by halogens (Saiz-Lopez et al., 2012a, 2014). Similarly, high levels of halogen-driven O₃ loss are also found in the upper troposphere (350 hPa > p > tropopause), with lower (10–15%) impacts in the free troposphere (350 hPa
- In order to explore our current understanding of the tropospheric chemistry of iodine 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 O₃ and OH

are described in Sect. 5. In Sect. 15 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

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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., 2012), and a mass-based aerosol scheme. Stratospheric chemistry is climatologically represented based on LINOZ McLinden et al. (2000) for O₃ and linearised chemistry is applied for other

species with concentrations taken from the Global Modelling Initiative (GMI) as described previously Murray et al. (2012).

lodine tracers (I₂, HOI, IO, OIO, HI, INO₂, INO₃, I, INO, CH₃I, CH₂I₂, CH₂IBr, CH₂ICl, I₂O₂, I₂O₃, I₂O₄ 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 model ("Br+I") 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.

As well as the core simulation present in this paper ("Br-I"), comparisons with the existing standard GEOS-Chem simulation ("BROMINE") are presented which contain bromine chemistry as described in Section 2.6. When considering the coupling of iodine and bromine two additional simulations are include, one with just iodine chemistry ("IODINE") and one with bromine or iodine chemistry ("NOHAL').

For budgets and general analysis we run the model at $2^{\circ} \times 2.5^{\circ}$ resolution for two years (2004 and 2005) discarding the 1st "spin up" year and using the final year (2005) for analysis

and budgets. For the sensitivity study (Section 7) the model is run with the same period for "spin up" and analysis, but at $4^{\circ} \times 5^{\circ}$ resolution. The model output is discussed with focus on the marine boundary layer (900 hPa <p); the free troposphere (350 hPa < p < 900 hPa); and upper troposphere (350 hPa > p > tropopause). Comparisons with observations involve separate spin-up simulations, run with the date appropriate meteorology, sampled at the spatially and temporally nearest grid box and time step. We report here mixing ratios as pmol/mol or nmol/mol, which are equivilent to more widely used pptv/ppbv.

2.1 lodine emissions

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Both organic and inorganic iodine species (Table 1 and Figure 1) are emitted into the atmosphere. Monthly emissions of organic iodine compounds (CH₃I, CH₂I₂, CH₂IBr, and CH₂ICI) are taken from Ordóñez et al. (2012) which parametrises fluxes based on chlorophyll a in the tropics and constant oceanic fluxes with 2.5 coast-to-ocean emission ratios for extratropical regions, and follows Bell et al. (2002) for CH₃I. Inorganic iodine compounds (HOI, I₂), formed from the uptake of O₃ to the ocean and the subsequent ocean surface reaction

- of O₃ with iodide (I⁻), are emitted as calculated from Eqs. (19) and (20) in Carpenter et al. (2013). We parameterise ocean surface I⁻ concentration from the sea surface squared temperature relationship in Table 2 from Chance et al. (2014), the O₃ concentration in the lowermost level of the model, and the 10 m wind speed from meteorological fields. The 10m wind speed used by the parameterisation is limited to a minimum of 5m/s to prevent unsubstantiated emissions at low wind speeds. Annual average iodine emission fluxes are shown
- in Figure 1.
 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 47 % higher than 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 O₃ concentration the largest differences lie in the choice of parameterisation for sea surface iodide (see Sect. 7.5).

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2.2 Iodine deposition

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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, 2015). This approach is applied to I_2 , HI, HOI, INO₂, INO₃, I_2O_2 , I_2O_3 and I_2O_4 . Aerosol iodine is assumed to have the same wet deposition properties as sulfate aerosol.

Wet deposition is calculated for I₂, HI, HOI, INO₂, INO₃, I₂O₂, I₂O₃, and I₂O₄ for both large scale (frontal) and convective rain by applying scavenging in and below clouds (Liu et al., 2001) using species-specific values for Henry's law coefficients (Sander, 2015; Vogt et al., 1999) and molar heats of formation (Kaltsoyannis and Plane, 2008; Sander, 2015) 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 dry deposition properties as sulfate aerosol.

15 2.3 lodine 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, INO₂, INO₃) 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). Crosssections 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 INO₃, an approach used previously (Bloss et al., 2010). For most species (I_2 , HOI, IO, OIO, INO, INO₂, I_2O_2 , CH₃I, CH₂I₂, CH₂IBr and CH₂ICI) we assume a quantum yield of 1, but for INO₃ we use a quantum yield of 0.21 (Sander et al., 2011).

2.5 Heterogeneous processes

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In line with previous studies (McFiggans et al., 2000), we consider that the uptake of HOI, INO₂ and INO₃ leads to the recycling of iodine back into the gas phase as $\frac{1}{2}$ I₂ on sea-salt aerosol alone, whereas irreversible loss via uptake of HI leads to the generation of aerosol phase iodine. Uptake of I₂O_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 (γ). Reactions considered and values of γ used are based on recommendations and previous studies (see Table 6 and Sect. A1.2).

15 2.6 Model bromine chemistry

The bromine simulation in GEOS-Chem is described in Parrella et al. (2012) and this bromine chemistry is included in the simulations "BROMINE" and "Br-I" in 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 (900 hPa <p) (~ 2 pmol/mol, Read et al., 2008) by a ratio of ~ 5 (0.4 pmol/mol). We consider the uncertainty in BrO concentration on our simulation as a part of our sensitivity study in Sect. 7.

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3 lodine model results and observation comparisons

In this section we describe and evaluate our iodine simulation ("Br+I"), which includes both iodine and bromine chemistry (Section 2.6). 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

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Figures 2 and 3 show annually averaged zonal (Fig. 2) and surface concentrations (Fig. 3) of organic and inorganic iodine precursors and their degradation products. These figures clearly illustrate the oceanic nature of iodine source species (CH₃I, CH₂I₂, CH₂ICI, CH₂IBr, HOI, I₂), with the highest concentrations over the tropical ocean. These plots also highlight the contribution of the included terrestrial CH₃I paddy field source (25%) to global CH₃I 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 CH₃I and CH₂ICI (Fig. 4) 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 as described in Andrews et al. (2015), using whole air samples from the Facility Airborne Atmospheric Measurement 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 CH₃I concentrations (Fig. 4). Concentrations of CH₂ICI appear to be better simulated in marine boundary layer (900 hPa <p) where measurements are available (Fig. 4). Although not definitive, this brief comparison suggests the model, if anything, underestimates the concentration of organic iodine.</p>

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 pmol/mol 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 pmol/mol. Some component of this overestimate probably relates to the model's iodine heterogenous recycling which assumes 100 % conversion of HOI, INO₃, and INO₂ into $\frac{1}{2}$ I_2 rather than ICI and IBr which has been observed in laboratory studies (Braban et al., 2007).

10 3.2 Iodine oxide (IO) observations

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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. 5. Good agreement is seen in the West Pacific (TransBrom, Großmann et al., 2013) and tropical 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, TORERO ship Volkamer et al., 2015).

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 $\sim +50$ to 250 %), TORERO ship observations (bias +114 - 164 %), and both under- and over- estimates values from the HALOCast-P cruise (bias ~ -0.92 to 280 %). When all observations are latitudinally aver-

HALOCast-P cruise (bias ~ -0.92 to 280 %). When all observations are latitudinally averaged (onto a 20° grid) a median bias of $\sim +90$ % is found.

In Fig. 6 we show a comparison with recent aircraft IO observations from the TORERO aircraft 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 overestimates the observations (average bias of +82 % within the binned comparison). Biases in the comparison are greatest (bias = +125 %) in the marine boundary layer (900 hPa <p) and lowest (bias = +73 %) in Discussion Paper

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the free troposphere (350 hPa hPa). The median bias in the upper troposphere (350 hPa <math display="inline">> p > tropopause) 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 analyse modelled distribution the of iodinated compounds. We now 10 the phase inorganic iodine species $(2I_2 + HOI)$ start with total gas ly $+10 + 010 + HI + INO + INO_2 + INO_3 + 2I_2O_2 + 2I_2O_3 + 2I_2O_4)$ and then move to the distribution of the IO_X (I + IO) family.

4.1 Total inorganic iodine (I_Y)

The modelled iodine system is schematically shown in Fig. 7. lodine emissions total 3.8 Tg l yr⁻¹ with most of this (3.2 Tg l 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 l yr⁻¹ (Saiz-Lopez et al., 2012a) and 2.6 Tg l 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 l yr⁻¹ (Ordóñez et al., 2012), and 0.65 Tg l 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 × 10⁸ atoms (I) cm⁻² s⁻¹. This value is to-wards 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).

Annual mean surface concentrations (Fig. 3) of IO are ubiquitously found over the oceans at ($\sim 0.25 - 1 \text{ pmol/mol}$). Minor species (e.g. HI, OIO) are modelled at greatest mixing ratios over the tropical oceans and towards the poles. lodine compounds formed through interacts with NO_X (INO₃/INO₂) peaking in the northern hemisphere in polluted oceanic regions. However due to limited or non-existent measurements of these species in the remote 5 marine boundary layer, these species offer limited ability to constrain the modelled values. lodine deposition is predominantly through HOI (51%). The remainder is mostly through deposition of INO₃ (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 tro-10 posphere. 350 hPa > p > tropopause) this can increase by three orders of magnitudes. Figures 8 and 9 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 (CH₂IX (where X = CI, Br, I) and I₂) are negligible 15 outside of the lowest model levels but the concentrations of others (CH₃I and HOI) persist further through the column. For CH₃I this is due to its longer lifetime of ~ 4 days. However, the lifetime of HOI is short ($\sim 4 \min$) and its persistence at higher altitudes reflects secondary chemical sources. From the top of the boundary layer to $\sim 10 \, \text{km}$ the I_Y profile is flat due to the rapid convective mixing within the tropics, however above this mixing zone 20 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 vr⁻¹) and organic iodine photolysis $(7.9 \,\mathrm{Gg\,yr^{-1}})$, overwhelmingly of CH₃I. Overall, atmospheric

 $_{25}$ greatest fraction (~70 %) in the free troposphere (350 hPa $\, hPa).$

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 HO₂ (77%),

iodine is dominated by three IOy species (HOI, IO, and INO₃) with HOI representing the

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 > p > tropopause) (up to 9 times) and ⁵ beyond latitudes of 80° N and S (up to 4 times) due to colder temperatures. The major IO formation route (I + O₃) 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 > p > 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 sourced from photolysis of transported organic iodine species and direct transport of I_Y .

5 Impact of iodine on O₃ and OH

O₃ 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 O₃

²⁰ On inclusion of iodine, the calculated global tropospheric O_3 burden drops from 367 to 334 Tg (9.0%). Figure 10 shows the annual average tropospheric column, surface and zonal change in O_3 . On average the O_3 burdens in the marine boundary layer (900 hPa <p) decreased by 19.5%, by 9.8% the free troposphere (350 hPa < p < 900 hPa), and 6.2% in the upper troposphere (350 hPa > p > tropopause). The decrease is greater in the Southern Hemisphere (9.5%), than the Northern Hemisphere (8.5%).

Surface (lowermost model level) O_3 shows an average decrease of 3.5 nmol/mol globally, with large spatial variability (Fig. 11) with a 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. 11), 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 12 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 nmol/mol). As with comparison of surface observations (Fig. 12), 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 south of 60° S at the surface where bias are increased and in the tropical free troposphere (350 hPa $hPa) where model <math>O_3$ biases are to decreased.

5.2 O₃ budget

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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 defined in Footnote 1.

- lodine provides a global tropospheric O_X loss of 748 Tg yr⁻¹ (15% of the total). This is significantly larger than the 178 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 HO₂. The O₃ production term increases slightly (~1%) with the inclusion of iodine reflecting small changes in the total reactive nitrogen partitioning.
- ²⁵ Iodine induced O₃ loss within the marine (land mask applied and between 50° N–50° S) troposphere of ~ 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 (~ 500 Tg yr⁻¹).

Figure 13 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 > p > tropopause), iodine represents 33 and 26% of the total loss, respectively. The loss within the marine boundary layer (900 hPa < p) is comparable to the 28% reported in 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. 8 and 9). In the upper troposphere, higher IO_X and BrO_X concentrations lead to increased loss of O_3 .

Figure 14 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 larger ocean area in the Southern Hemisphere increasing emissions. Convective transport in the tropics rapidly lifts iodine species into the free troposphere (350 hPa O_3.

5.3 Impact on OH

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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 HO₂ to OH. However we find that the inclusion of iodine in the model has little impact on the global mean OH concentrations with it slightly increasing from 12.2 to 12.5×10^5 molecules cm⁻³(1.8%). This small increase is surprising given the 12% reduction in the primary source (O₃ + H₂O + h ν) due to lower O₃ concentrations. However, this is more than 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 O₃ loss has been previously highlighted and found to be required to replicate observed diurnal surface O₃ 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 ("IODINE") and one without any halogens ("NOHAL").

As shown in Table , the global tropospheric burdens of O_3 are 390, 367 (reduction of 5.9%), 357 (8.5%) and 334 Tg (14%) for the simulations without halogens ("NOHAL"), with just bromine ("BROMINE"), with just iodine ("IODINE"), and with both iodine and bromine chemistry ("Br+I") respectively. The sum of the changes in O_3 burden for the runs considering halogens individually is slightly lower (0.1%) than when considered simultaneously.

Figure 15 shows the combined daily surface loss rate of O₃ driven by bromine and iodine
(upper panel). This correlates with IO concentrations (Fig. 3) reflecting iodine's role in marine boundary layer O₃ destruction. Figure 15 also shows modelled and observed fractional diurnal fractional O₃ change at Cape Verde in the remote marine boundary layer (lower panel). For this comparison, observations (2006 to 2012, (Sofen et al., 2015)) and model data were first processed to average fractional diurnal change by averaging the values by hour of day, then subtracting the maximum average value of the diurnal. This fractional change was then divided by the average maximum value and multiplied by 100 to give % allow comparison between simulation runs with different O₃ concentrations.

The simulation's fidelity increases significantly with the inclusion of iodine (Fig. 15) but there is little impact from bromine. Whereas modelled IO concentrations at Cape Verde shows agreement with observations (Fig. 5), BrO concentrations (~ 0.4 pmol/mol) are significantly lower than reported (~ 2 pmol/mol, 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 ("NOHAL"), with just bromine ⁵ ("BROMINE"), with just iodine ("IODINE"), and with both iodine and bromine chemistry ("Br+I") 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. 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 (O₃ + H₂O + h ν) from a reduced O₃ burden. The net impact overall on inclusion of halogens is a global reduction in OH (2.6%).

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° × 5° 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 "Br+I" simulation described in Sects. 2–5.
Figure 17 summarises the fractional impact of these experiments on the globally averaged
vertical distribution of I_Y, O₃ and vertical profile comparison of observations of IO from the TORERO aircraft campaign (Volkamer et al., 2015; Wang et al., 2015). Additional information is listed in Table A1 in the Appendix A.

7.1 Just Organic lodine

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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 (65%), and mean surface marine boundary layer (900 hPa<p) IO decreases (83%). The median bias against TORERO aircraft IO observations decreases by 68% to become a negative bias of -25%. The decreased I_Y leads to the mean global OH decreasing by 0.64% and global tropospheric O₃ increasing by 5.5%.

10 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 a heterogeneous recycling of unity (e.g. HOI $\rightarrow \frac{1}{2}I_2$) 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 γ chosen is in Appendix A (Section A1.2). To explore these uncertainties four simulations were run: (1) with the γ values that lead to I₂ release doubled ("het. cycle $\times 2$ "), (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 $\times 2$ ") converts more HOI (the dominant I_Y species) into I₂, thus reducing the rate of HOI deposition. The global I_Y burden increases by 6%, mean surface marine boundary layer (900 hPa <p) IO concentration increases by 2% and the median bias with respect to the TORERO aircraft IO observations increases by

²⁵ 26 to 100 % (Fig. 17). 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 aircraft 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 boundary layer (900 hPa <p) IO concentration decreases by 48 and 22 %. The median bias with respect to the TORERO aircraft 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 aircraft IO observations to be negative, instead of positive (+80 % for "Br+I" at 4° × 5°).

This large decrease in I_Y reduces the potency of iodine chemistry. The reductions in the tropospheric O₃ 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

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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 (I₂O₂, I₂O₃, I₂O₄) are highly uncertain (Bloss et al., 2001; Gómez Martín et al., 2005; Spietz et al., 2005) and we use the INO₃ spectrum in our simulation. This uncertainty was tested in 3 simulations: (1) absorption cross-sections were doubled ("I₂O_X X-sections ×2"), (2) tentative literature assignments of spectra were used for I₂O₃ and I₂O₂ (Bloss et al., 2001; Gómez Martín et al., 2005; Spietz et al., 2005), with I₂O₂ used for I₂O₄ (" I_2O_X exp. X-sections"), (3) and finally no I_2O_X photolysis at all was considered ("No I_2O_X photolysis").

Sensitivity runs " I_2O_X X-sections $\times 2$ " 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

- ⁵ by 3.1 and 4.8% respectively. The average surface marine boundary layer (900 hPa<p) IO concentration responds by increasing by 4.3 and 6.7% for "I₂O_X X-sections ×2" and "I₂O_X exp. X-sections" respectively. Both these simulation increase median bias with TORERO aircraft IO observations by 4.8 to 84% and 7.6 to 86%, respectively. The impacts on O₃ burden are small with a decrease of 0.4 and 0.6% for "I₂O_X X-sections ×2" and "I₂O_X
 ¹⁰ exp. X-sections" respectively. Global mean OH concentrations increase by 0.05 and 0.09%
 - respectively.

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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 <p) IO (40%), increases tropospheric O₃ burden (5.1%) and decreases global mean OH (0.9%) with respect to "Br+I". The median bias with respect to the TORERO aircraft 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. 17). 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 "Br+I". Saiz-Lopez et al. (2014) find a decrease in marine tropospheric O₃ 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 %.

25 7.4 Marine boundary layer BrO concentration

As discussed in the introduction and Sect. 15, bromine and iodine chemistry are potentially coupled. GEOS-Chem underestimates BrO (Parrella et al., 2012), with for example, our

simulation underestimating the BrO concentrations at Cape Verde (Read et al., 2008) (\sim 2 pmol/mol) by a factor of around 5.

- To test the sensitivity of the model to BrO concentrations, a simulation with BrO concentration fixed at 2 pmol/mol in the daytime marine boundary layer was run ("MBL BrO 2 pmol/mol"). Increased BrO leads to increased OIO concentrations (BrO + IO \rightarrow OIO + Br), 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 aircraft IO observations decreases by 12 to 71%. Although the overall tropospheric O₃ burden decreases by 3.7%, the average O₃ change at the surface is larger and shows a decrease of 88% (Fig. 17) which is the largest decrease in O₃ found within these
- ¹⁰ shows a decrease of 88 % (Fig. 17) which is the largest decrease in O₃ 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
¹⁵ 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 16 shows annual averaged ocean surface iodide generated from both parameterisations. The sea surface temperatures are taken from the annual mean GEOS field used in GEOS²⁰ 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 differences apparent in magnitude. The dataset reported in Chance et al. (2014) has a median value of 77 nM and interguartile range of 28–140 nM.

²⁵ 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 "Br+I".

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 INO₂ (0.02). 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 <p) IO (4.6 %), and decreases the median bias in vertical comparisons with TORERO aircraft IO (6.9 %) to 75 %. This leads to a slightly increased global tropospheric O₃ 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 <p) IO concentration (4.3 %), and an increased median bias in vertical comparisons with TORERO aircraft IO by 4.4 to 84 %. This leads to slightly decreased global tropospheric O₃ burden (0.05 %).

7.7 Summary of sensitivity simulations

Uncertainties in the atmospheric chemistry of iodine lead to some significant uncertainties on iodine's impact on 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 emissions' 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 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

⁵ We find this dominated by the inorganic ocean source (84%), and 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 -H₂O primary source being compensated for by an increased conversion of HO₂ 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 O₃ 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 O₃ destruction and HO₂ to IO cycling, a priority should be given to instrumentation to measure HOI.

Appendix A:

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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 ²⁵ 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 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.

 $M5-HOI+OH \rightarrow IO+H_2O$

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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).

 $M12{-}INO_3{+}I{\rightarrow}I_2{+}NO_3$

This reaction's rate is based on a single theoretical study (Kaltsoyannis and Plane, 2008). The impact of inclusion within a box model was found to be minimal, except in high iodine and NOx conditions (Sommariva et al., 2012).

 ${}_{^{15}}\quad M17{-}OIO+OIO\rightarrow I_2O_4$

This reaction rate is from a single experimental study (Gómez Martín et al., 2007), which yielded a lower limit of $1.2 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. This reaction is included in this work, along with the reverse reaction (Reaction M24, $I_2O_4 \rightarrow 2OIO$).

 $\mathsf{M26-INO_3} \xrightarrow{\mathsf{M}} \mathsf{IO} + \mathsf{NO_2}$

²⁰ The reaction is included in the IUPAC (Atkinson et al., 2007) without direct experiment observation. No recommendation is given in the recent JPL compilation (Sander et al., 2011). The INO₃ thermal stability used by studies has led significant range between reaction rates (298 K) from 1.08×10^{-2} (Read et al., 2008) to 2.51×10^{-5} cm³ molecules⁻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 M25) has been included ubiquitously in iodine modelling work; and reverse reaction (Reaction M26) is employed in the majority of, but not all studies (Ordóñez et al., 2012). Both reactions are included in this work.

 $M21{-}IO + OIO \xrightarrow{M} I_2O_3$

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A single experimental study (Gómez Martín et al., 2007) gives a upper limit and lower rate limit of 1.5×10^{-10} and 1.5×10^{-11} cm³ molecules⁻¹ s⁻¹, respectively. We use the higher value in this work as in others studies (Saiz-Lopez et al., 2008; Sommariva et al., 2012).

¹⁰ M22-I₂O₂
$$\xrightarrow{M}$$
 IO + IO
M23-I₂O₂ \xrightarrow{M} OIO + I

These reaction has been studied solely theoretically (Kaltsoyannis and Plane, 2008). A temperature dependent rate was calculated theoretically (Ordóñez et al., 2012) which is used in our work.

15 M24-I₂O₄ \xrightarrow{M} 2010

The rate is calculated from the value for binding energy of the dimer (Kaltsoyannis and Plane, 2008). As have included reaction M17 (OIO + OIO \rightarrow I₂O₄), we also include the reverse Reaction M24 in our work at the Kaltsoyannis and Plane (2008) rate.

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

As described in Sect. 3.1, we stoichiometrically emit I₂ following uptake of species that hydrolyse to HOI (INO₂, INO₃, HOI). We assume this to avoid double counting of Br 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 H₂SO₄, yielding mass accommodation coefficients (α) in the range 0.02 to 0.07 (Sander et al., 2011). ⁵ Another two studies on ice and salt are reported in JPL 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 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 INO₂ and INO₃ no experiment work is available on the uptake and values have previously been estimated by analogy with measured equivalent bromine species. For INO₃ a γ value of 0.01 has been frequently used based on estimations (Mahajan et al., 2009;

- ¹⁵ 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 INO₂ 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 INO₃ and INO₂ 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 though has most often been used in modelling studies (Breider, 2010; Mahajan et al., 2009; Saiz-Lopez et al., 2008) and 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 INO₂. 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.

Acknowledgements. This work was funded by NERC quota studentship NE/K500987/1 with support from the NERC BACCHUS and CAST projects NE/L01291X/1, NE/J006165/1.

R. Volkamer acknowledges funding from US National Science Foundation CAREER award ATM-0847793, AGS-1104104, and AGS-1452317. The involvement of the NSF-sponsored Lower Atmospheric Observing Facilities, managed and operated by the National Center for Atmospheric Research (NCAR) Earth Observing Laboratory (EOL), is acknowledged.

T. Sherwen would like to acknowledge constructive comments from and conversations with all coauthors as well as R. Chance and J. Schmidt.

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Species	Emissions Tg I yr $^{-1}$
CH₃I	0.26
CH_2I_2	0.11
CH_2ICI	0.18
CH_2IBr	0.05
I_2	0.32
HOI	2.91
Total	3.83

 Table 1. Total simulated emissions for iodinated species.

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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 $(1 \times 10^{20} \text{ M} \text{ atm}^{-1})$. The INO₂ Henry's law constant is assumed equal to that of BrNO₃, from Sander (2015), by analogy. For I₂O_X ($_X = 2, 3, 4$) a Henry's law constant of infinity is assumed by analogy with INO₃. (*) Effective henry's law of HI is calculated for acid conditions through $K_H^*(T) = K_H(T) \times (1 + \frac{K_a}{[H^+]})$, where $K_a = 1 \times 10^9$ M is the acid dissociation constant (Bell, 1973).

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 (2015)	-8.37×10^3	Sander et al. (2006)
D2	HI	$2.35 imes 10^{0}(*)$	Sander (2015)	-3.19×10^3	Sander et al. (2006)
D3	INO ₃	∞	Vogt et al. (1999)	$-3.98 imes10^4$	Kaltsoyannis and Plane (2008)
D4	I_2O_2	∞	see caption text	$-1.89 imes10^4$	Kaltsoyannis and Plane (2008)
D5	I_2	$2.63 imes10^{0}$	Sander (2015)	$-7.51 imes10^3$	Sander et al. (2006)
D6	INO_2	$3.00 imes10^{-1}$	see caption text	$-7.24 imes10^3$	Sander et al. (2006)
D7	I_2O_3	∞	see caption text	$-7.70 imes10^3$	Kaltsoyannis and Plane (2008)
D8	I_2O_4	∞	see caption text	-1.34×10^{4}	Kaltsoyannis and Plane (2008)

Table 3. Bimolecular and unimolecular 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. The bi-molecular reactions with an M in them represent termolecular reactions where the pressure dependence is not known or are uni-molecular decomposition reactions. Reactions included, but not in IUPAC/JPL are discussed further in Section A1.1.

Rxn ID	Reaction	A	Ea/R	Citation
		$\mathrm{cm}^3\mathrm{molecules}^{-1}\mathrm{s}^{-1}$	К	
M1	$I + O_3 \rightarrow IO + O_2$	2.10×10^{-11}	-830	Atkinson et al. (2007)
M2	$I + HO_2 \to HI + O_2$	$1.50 imes10^{-11}$	-1090	Sander et al. (2011)
M3	${\sf I}_2 + {\sf OH} \rightarrow {\sf HOI} + {\sf I}$	$2.10 imes10^{-10}$	-	Atkinson et al. (2007)
M4	$HI+OH \rightarrow I+H_2O$	$1.60 imes10^{-11}$	440	Atkinson et al. (2007)
M5	$\text{HOI} + \text{OH} \rightarrow \text{IO} + \text{H}_2\text{O}$	$5.00 imes10^{-12}$	-	Riffault et al. (2005)
M6	$\text{IO} + \text{HO}_2 \rightarrow \text{HOI} + \text{O}_2$	$1.40 imes10^{-11}$	540	Atkinson et al. (2007)
M7	$\text{IO} + \text{NO} \rightarrow \text{I} + \text{NO}_2$	$7.15 imes 10^{-12}$	300	Atkinson et al. (2007)
M8	$\rm HO + CH_3I \rightarrow H_2O + I \ (CH_2I)$	$4.30 imes 10^{-12}$	-1120	Atkinson et al. (2008)
M9	$\text{INO} + \text{INO} \rightarrow \text{I}_2 + 2\text{NO}$	$8.40 imes 10^{-11}$	-2620	Atkinson et al. (2007)
M10	$INO_2 + INO_2 \to I_2 + 2NO_2$	$4.70 imes 10^{-12}$	-1670	Atkinson et al. (2007)
M11	$I_2 + NO_3 \to I + INO_3$	$1.50 imes 10^{-12}$	-	Atkinson et al. (2007)
M12	$INO_3 + I \rightarrow I_2 + NO_3$	$9.10 imes 10^{-11}$	-146	Kaltsoyannis and Plane (2008)
M13	$I + BrO \rightarrow IO + Br$	$1.20 imes 10^{-11}$	-	Sander et al. (2011)
M14	$IO + Br \rightarrow I + BrO$	$2.70 imes 10^{-11}$	-	Bedjanian et al. (1997)
M15	$\text{IO} + \text{BrO} \rightarrow \text{Br} + \text{I} + \text{O}_2$	$3.00 imes 10^{-12}$	510	Atkinson et al. (2007)
M16	$IO + BrO \rightarrow Br + OIO$	$1.20 imes 10^{-11}$	510	Atkinson et al. (2007)
M17	$\text{OIO} + \text{OIO} \rightarrow \text{I}_2\text{O}_4$	$1.50 imes10^{-10}$	-	Gómez Martín et al. (2007)
M18	$OIO + NO \rightarrow NO_2 + IO$	$1.10 imes 10^{-12}$	542	Atkinson et al. (2007)
M19	$IO + IO \rightarrow I + OIO$	$2.16 imes 10^{-11}$	180	Atkinson et al. (2007)
M20	$IO + IO \xrightarrow{M} I_2O_2$	3.24×10^{-11}	180	Atkinson et al. (2007)
M21	$IO + OIO \xrightarrow{M} I_2O_3$	1.50×10^{-10}	-	Gómez Martín et al. (2007)
M22	$I_2O_2 \xrightarrow{M} IO + IO$	1.00×10^{12}	-9770	Ordóñez et al. (2012)
M23	$I_2O_2 \xrightarrow{M} OIO + I$	2.50×10^{14}	-9770	Ordóñez et al. (2012)
M24	$I_2O_4 \xrightarrow{M} 2OIO$	3.80×10^{-2}	-	Kaltsoyannis and Plane (2008)
M25	$INO_2 \xrightarrow{M} I + NO_2$	9.94×10^{17}	-11859	McFiggans et al. (2000)
M26	$INO_3 \xrightarrow{M} IO + NO_2$	2.10×10^{15}	-13670	Kaltsoyannis and Plane (2008)

Table 4. Termolecular iodine reactions. The lower pressure limit rate (k_0) is given by: $A_0 \cdot \exp(\frac{Ea}{RT}) \cdot (\frac{300}{T})^x$. The high pressure limit is given by k_{∞} . 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.

Rxn ID	Reaction	$\stackrel{A_0}{\mathrm{cm}^6\mathrm{molecules}^{-2}\mathrm{s}^{-1}}$	$\frac{Ea/R}{\rm K}$	x	$\overset{k_{\infty}}{\mathrm{cm}^{3}\mathrm{molecules}^{-1}\mathrm{s}^{-1}}$	Fc	Citation
T1	$I + NO + M \to INO + M$	1.80×10^{-32}	300	1	$1.70 imes 10^{-11}$	0.60	Atkinson et al. (2007)
T2	$I + NO_2 + M \to INO_2 + M$	$3.00 imes 10^{-31}$	300	1	$6.60 imes 10^{-11}$	0.63	Atkinson et al. (2007)
Т3	$\rm IO + \rm NO_2 + \rm M \rightarrow \rm INO_3 + \rm M$	7.70×10^{-31}	-	5	1.60×10^{-11}	0.40	Atkinson et al. (2007)

Reaction	Reference cross-section
$I_2 + h\nu \rightarrow 2I$	Sander et al. (2011)
HOI + h u ightarrow I + OH	Sander et al. (2011)
$IO + h\nu \rightarrow I + [O_3]$	Sander et al. (2011)
$OIO + h\nu \rightarrow I + O_2$	Sander et al. (2011)
$INO + h\nu \rightarrow I + NO$	Sander et al. (2011)
$INO_2 + h\nu \rightarrow I + NO_2$	Sander et al. (2011)
$INO_3 + h\nu \rightarrow I + NO_3$	Sander et al. (2011)
$I_2O_2 + h\nu \rightarrow I + OIO$	see caption
$CH_3I + h\nu \rightarrow I + CH_2O_2$	Sander et al. (2011)
$CH_2I_2 + h\nu \rightarrow 2I + (CH_2)$	Sander et al. (2011)
$CH_2ICI + h\nu \rightarrow I + (CH_2CI)$	Sander et al. (2011)
$CH_2IBr + h\nu \rightarrow I + (CH_2Br)$	Sander et al. (2011)
I_2O_4 + $h\nu \rightarrow 2OIO$	see caption
$I_2O_3 + h\nu \rightarrow OIO + IO$	see caption
	$\begin{array}{l} \mbox{Reaction} \\ \hline I_2 + h\nu \rightarrow 2I \\ \mbox{HOI} + h\nu \rightarrow I + OH \\ \mbox{IO} + h\nu \rightarrow I + O3 \\ \mbox{IOO} + h\nu \rightarrow I + O2 \\ \hline INO + h\nu \rightarrow I + NO \\ \mbox{INO}_2 + h\nu \rightarrow I + NO2 \\ \hline INO_3 + h\nu \rightarrow I + NO3 \\ \hline I_2O_2 + h\nu \rightarrow I + OIO \\ \hline CH_3I + h\nu \rightarrow I + CH_2O2 \\ \hline CH_2I_2 + h\nu \rightarrow 2I + (CH_2) \\ \hline CH_2ICI + h\nu \rightarrow I + (CH_2CI) \\ \hline CH_2IBr + h\nu \rightarrow I + (CH_2Br) \\ \hline I_2O_4 + h\nu \rightarrow 2OIO \\ \hline I_2O_3 + h\nu \rightarrow OIO + IO \end{array}$

Table 5. Photolysis reactions of iodine species. For I_2O_X ($_X = 2,3,4$) the cross-section of INO₃ is used as described in Sect. 2.4.

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	$\text{HI} \rightarrow \text{iodine aerosol}$	0.10*	Crowley et al. (2010)
K2	$INO_3 \to 0.5I_2$	0.01*	see caption text
K3	$\text{HOI} \rightarrow 0.5\text{I}_2$	0.01*	Sander et al. (2011)
K4	$INO_2 \to 0.5I_2$	0.02*	see caption text
K5	$I_2O_2 \rightarrow \text{iodine aerosol}$	0.02	see caption text
K6	$I_2O_4 \rightarrow \text{iodine aerosol}$	0.02	see caption text
K7	$I_2O_3 \rightarrow \text{iodine aerosol}$	0.02	see caption text

Table 7. Comparison between global tropospheric O_X budgets of simulations "BROMINE", "Br+I", "IODINE" and "NOHAL" are described here. "BROMINE" includes just bromine chemistry, "Br+I" which includes both iodine and bromine chemistry, "IODINE" only includes iodine chemistry, and "NOHAL" is simulation without iodine or 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	"NOHAL"	"IODINE"	"BROMINE"	"Br+I"	ACCENT Young et al. (2013)
O ₃ burden (Tg)	390	357	367	334	340 ± 40
O _X chemical Sources (Tg Yr ⁻¹)					
$NO + HO_2$	3667	3680	3512	3529	-
NO + CH_3O_2	1332	1383	1269	1307	-
Other O _X sources	502	518	505	521	-
Total chemical O _X sources (PO _X)	5501	5581	5286	5357	5110 ± 606
O _X chemical sinks (Tg Yr ⁻¹)					
$O_3 + h\nu + H_2O \rightarrow 2OH + O_2$	2579	2271	2425	2119	-
$O_3 + HO_2 \rightarrow OH + O_2$	1391	1186	1274	1080	-
$O_3 + OH \rightarrow HO_2 + O_2$	687	627	621	560	-
$HOBr + h\nu \rightarrow Br + OH$	-	-	166	143	-
HOBr + HBr \rightarrow Br ₂ + H ₂ O (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	-
$HOI + h\nu \rightarrow I + OH$	-	639	-	583	-
$HOI \rightarrow 0.5I_2$ (seasalt aerosol)	-	2	-	2	-
$IO + BrO \rightarrow Br + I + O_2$	-	-	-	7	-
$OIO + h\nu \rightarrow I + O_2$	-	114	-	156	-
Other iodine O _X sinks	-	1	-	1	-
Total iodine O_X sinks	-	756	-	748	-
Other O _X sinks	176	181	172	179	-
Total chem. O_X sinks (LO _X)	4833	5021	4687	4864	4668 ± 727
$O_3 P(O_X)-L(O_X) (Tg Yr^{-1})$	668	560	599	493	618 ± 251
O ₃ Dry deposition (Tg Yr ⁻¹)	949	850	886	791	1003 ± 200
O ₃ Lifetime (days)	25	22	24	22	22 ± 2
O_3 STE (PO _X -LO _X -Dry dep.) (Tg Yr ⁻¹)	281	290	287	298	552 ± 168

Table A1. Effects of sensitivity runs on relevant variables. Values are shown as percentage change from the simulation with both iodine and bromine chemistry ("Br+I") in the troposphere as global means unless otherwise stated. MBL = Marine Boundary Layer (900 hPa <p), O_X is defined as in Footnote 1. CH₄ 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
NOHAL	-100.00	2.34	-0.75	40.91	15.99	17.75
BROMINE	-100.00	-1.79	-3.90	24.50	9.12	10.42
IODINE	9.63	3.87	2.89	16.16	6.90	6.87
Br-I	0.00	0.00	0.00	0.00	0.00	0.00
Just org. I	-83.45	-1.64	-3.11	17.69	5.53	7.19
$I_2O_X \log(\gamma) \times 2$	-4.26	-0.15	-0.28	1.61	0.54	0.59
$I_2O_X \log(\gamma)/2$	3.93	0.13	0.24	-1.34	-0.44	-0.52
Het. cycle (γ) $\times 2$	2.21	0.04	0.16	-1.61	-0.69	-0.56
Het. cycle $(\gamma)/2$	-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 $\times 2$	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 ₂ O _X Photolysis	-39.35	-1.10	-2.12	12.33	5.05	4.86
MBL BrO 2 pmol/mol	-6.78	-3.59	-2.71	-15.28	-3.73	-6.03

Table A1.	Continued.
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	OH mean	HO ₂ mean	HO_2	١ _Y	IO_X	١ _Y	CH_4
	concentration	concentration	/OH	lifetime	lifetime	burden	lifetime
NOHAL	2.49	8.44	5.81	-100.00	105.16	-100.00	-3.73
BROMINE	-1.65	5.72	7.50	-100.00	89.64	-100.00	0.80
IODINE	4.30	2.31	-1.91	-1.31	-1.82	6.96	-4.67
Br-I	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Just org. I	-0.64	3.53	4.19	123.92	16.09	-64.26	0.21
$I_2O_X \log(\gamma) \times 2$	-0.08	0.27	0.36	-8.38	-0.93	-5.08	0.03
$I_2O_X \log(\gamma)/2$	0.05	-0.22	-0.27	8.00	0.55	4.27	-0.01
Het. cycle (γ) $\times 2$	0.09	-0.39	-0.49	4.61	1.13	5.98	0.00
Het. cycle $(\gamma)/2$	-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 $\times 2$	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 pmol/mol	-3.31	-1.44	1.93	-3.72	3.33	-10.07	4.17



Figure 1. Annual mean surface fluxes for iodine precursors in the "Br+I" simulation in kg m⁻² s⁻¹



Figure 2. Annual mean zonal tropospheric mixing ratios for precursor and reactive iodine compounds (pmol/mol) in the simulation with both iodine and bromine chemistry ("Br+l"). No calculations of concentrations are made within the stratosphere and so that region is left blank.



Figure 3. Annual mean surface mixing ratios for precursor and reactive iodine (pmol/mol) in the simulation with both iodine and bromine chemistry ("Br+I").



Figure 4. 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 simulated values with both iodine and bromine chemistry ("Br+I") in red. Values are considered in 0.5 km bins, with observations and modelled values at the same location and time (as described in section 2) shown side-by-side around the mid point of each bin. The observations are from the FAAM BAE-146 research aircraft whole air samples analysed by Gas Chromatography-Mass Spectrometry (GC-MS). 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.



Figure 5. lodine oxide (IO) surface observations (red) by campaign compared against the simulation with both iodine and bromine chemistry ("Br+I", black). Cape Verde measurements are shown against hour of day and others are shown as a function of latitude. Values are considered in 20° bins, with observations and modelled values at the same location and time (as described in section 2) shown side-by-side around the mid point of each bin. Extents of bins are highlighted with grey dashed lines. 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), HaloCAST-P (East Pacific, Mahajan et al., 2012), and TORERO ship (East Pacific, (Volkamer et al., 2015)). 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 6. Vertical comparison of the simulation with both iodine and bromine chemistry ("Br+I") and measured iodine oxide (IO) during TORERO aircraft campaign (Volkamer et al., 2015; Wang et al., 2015). Model and observations are in red and black respectively. Values are considered in 0.5 km bins, with observations and modelled values at the same location and time (as described in section 2) shown side-by-side around the mid point of each bin. Measurements were taken aboard the NSF/NCAR GV research aircraft by the University of Colorado airborne Multi-Axis DOAS instrument (CU AMAX-DOAS) in the eastern Pacific in January and February 2012 (Volkamer et al., 2015; Wang et al., 2015) . 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.



Figure 7. Schematic representation of implemented iodine chemistry in the simulation with both iodine and bromine chemistry ("Br+I"). 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, and purple lines = depositional pathway. This equates to a total iodine source and sink of 3.8 Tg I yr^{-1} . O₃ deposition in Tg is also shown to illustrate the driving force behind the inorganic emissions.



Figure 8. Global annual mean gas-phase iodine speciation with altitude in the simulation with both iodine and bromine chemistry ("Br+I"). Mixing ratios are shown in pmol/mol, with higher iodine oxides (I_2O_X ($_X = 2,3,4$)) and di-halogenated organics (CH₂IX (X = CI, Br, I)) grouped.

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Figure 9. Zonal breakdown of global annual mean iodine speciation by family in the "Br+I" simulation. First panel shows total gas phase iodine concentration and the following panels show percentage of different compounds to this. Total gas phase iodine = $CH_3I + 2CH_2I_2 + CH_2IBr + CH_2ICI + 2I_2 + HOI + IO + OIO + HI + INO_2 + INO_3 + 2I_2O_2 + 2I_2O_3 + 2I_2O_4 + I + INO;$ $I_Y = 2I_2 + HOI + IO + OIO + HI + INO_2 + INO_3 + 2I_2O_2 + 2I_2O_4;$ $IO_X = I + IO.$



Figure 10. Decreases in annual mean tropospheric column, surface and zonal O_3 with inclusion of iodine ("Br+I"-"BROMINE") chemistry are shown on left, middle and right panels respectively. Upper panels show changes in Dobson units or nmol/mol and lower panels show changes in percentage terms.



Figure 11. 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 chemistry ("BROMINE") and green with inclusion of iodine chemistry ("Br+I").



Figure 12. 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. Red indicates standard GEOS-Chem (v9-2) including bromine chemistry ("BROMINE") and green with inclusion of iodine chemistry ("Br+I"). Observations (in black) show mean concentrations with upper and lower quartiles given by whiskers.



Figure 13. Vertical profile of simulated fractional global annual mean O_X loss by route in the "Br+I" simulation. O_X definition is given in Footnote 1). 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 14. Global annual O_3 mean zonal chemical lifetime for different O_X loss routes (Photolysis, HO_X, Iodine, Bromine, and Total) in the "Br+I" simulation. Values are shown on a log on a scale.



Figure 15. Global annual mean surface $O_3 loss (nmol/mol day⁻¹) in the "Br+I" simulation from both$ $bromine and iodine (top). Comparison between modelled and observed fractional diurnal <math>O_3$ cycles at the Cape Verde Observatory for "NOHAL", "BROMINE", "IODINE" and "Br+I" simulations (bottom). Calculation is described in text Section . Diurnal changes are averaged over the whole dataset. Lines are black, purple, red, blue and green for mean of observations, "NOHAL", "BROMINE", "IODINE" and "Br+I" respectively. Individual years of observational data are shown in grey.



Figure 16. 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.



Figure 17. 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 (pmol/mol) calculated along the TORERO aircraft 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.