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https://doi.org/10.5194/acp-16-1161-2016

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


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Received: 29 June 2015 – Published in Atmos. Chem. Phys. Discuss.: 5 August 2015
Revised: 12 January 2016 – Accepted: 21 January 2016 – Published: 2 February 2016

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$_2$O$_X$, $X = 2, 3, 4$) chemistry, photolysis, deposition, and parametrized heterogeneous reactions. In comparisons with recent 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. Iodine 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 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$^1$ (748 Tg O$_X$ yr$^{-1}$) is 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 conversion of hydroperoxy radicals exceeds the decrease in OH primary production from the reduced O$_3$ concentration. We perform sensitivity studies on a range of parameters and conclude that the simulation is sensitive to choices in parametrization of heterogeneous uptake, ocean surface iodide, and I$_2$O$_X$ ($X = 2, 3, 4$) 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, 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.

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; PPN = peroxypropionyl nitrate, MPN = methyl peroxy nitrate, and MPN = peroxymethacryloyl nitrate.)
Young et al., 2013), and determines human and agriculture exposure to air quality pollutants such as O₃ 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 O₃ 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 O₃ and OH in the troposphere is coupled, and the central aspects 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 focused on its chemical destruction. O₃ is chemically lost in the troposphere predominantly through photolysis in the presence of water or its reactions with HO₂ and OH (Lelieveld and Dentener, 2000). However, bromine and iodine compounds have also been identified as additional sinks for O₃ 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 compounds 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; Sommerariva et al., 2012). Once emitted into the atmosphere, the highly labile iodinated precursors rapidly photolyse with lifetimes of seconds (e.g. I₂/HOI) to days (e.g. CH₃I) to release atomic iodine. The iodine can catalytically destroy O₃ by the reaction of O₃ + I to form IO, followed by secondary reactions (+HO₂, +IO, +NO₂, +BrO) which can regenerate atomic I without the abstracted oxygen. For instance IO reacts with HO₂, leading to HOI formation, and this is rapidly photolysed to reform I causing a net conversion of HO₂ to OH.

Much of the uncertainty in iodine chemistry involves the production and fate of their higher oxides (I₂O₃). These higher oxides are formed from a chain reaction of IO self-reactions (Sommariva et al., 2012):

\[
\begin{align*}
O_3 + I & \rightarrow IO + O_2 \quad (R1) \\
IO + IO & \rightarrow IO + I \quad (R2) \\
IO + IO & \rightarrow I_2O_2 \quad (R3) \\
IO + OIO & \rightarrow I_2O_3 \quad (R4) \\
OIO + OIO & \rightarrow I_2O_4. \quad (R5)
\end{align*}
\]

Due to their short lifetimes and low concentrations, measuring iodine species poses significant challenges and so the observational data set is sparse. For decades, measurements have focused on organic compounds and mainly CH₃I (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. CH₃I and CH₂IX, with X = Cl, 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, data sets of IO observations with extensive geographical coverage (Prados-Roman et al., 2015b; Volkamer et al., 2015; Wang et al., 2015).

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 localized chemical perturbations mainly through the use of box models.

When considered alongside bromine chemistry, box model studies have shown the magnitude of halogen-driven O₃ loss processes to be up to 45% (Mahajan et al., 2009; Read 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 et al., 2005a; 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; Volkmer 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 by of the order of ∼10% (Saiz-Lopez et al., 2012a, 2014). As in the

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box model studies, up to $\sim 30\%$ of the O$_3$ 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 O$_3$ loss are also found in the upper troposphere (350 hPa > p > tropopause), with lower (10–15%) impacts in the free troposphere (350 hPa < p < 900 hPa) (Saiz-Lopez et al., 2012a, 2014).

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 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 summarizes 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., 2012), and a mass-based aerosol scheme. Stratospheric chemistry is climatologically represented based on LINOZ McLinden et al. (2000) for O$_3$ and linearized 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$_3$I, CH$_3$I$_2$, CH$_3$IBr, CH$_3$ICl, I$_2$O$_2$, I$_2$O$_3$, I$_2$O$_4$, and “aerosol iodine”) are included in the model. The modelled emissions, deposition, chemistry, photoysis, 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$_2$O$_X$ (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 Sect. 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 includes bromine chemistry as described in Sect. 2.6. When considering the coupling of iodine and bromine, two additional simulations are included, one with just iodine chemistry (“IODINE”) and one with no bromine or iodine chemistry (“NOHAL”).

For budgets and general analysis we run the model at $2^\circ \times 2.5^\circ$ resolution for 2 years (2004 and 2005) discarding the first “spin up” year and using the final year (2005) for analysis and budgets. For the sensitivity study (Sect. 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$^{-1}$ or nmol mol$^{-1}$, which are equivalent to the more widely used pptv or ppbv.

#### 2.1 Iodine emissions

Both organic and inorganic iodine species (Table 1 and Fig. 1) are emitted into the atmosphere. Monthly emissions of organic iodine compounds (CH$_3$I, CH$_3$I$_2$, CH$_3$IBr, and CH$_3$ICl) are taken from Ordóñez et al. (2012) which parametrizes 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 CH$_3$I. 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 parametrize ocean surface I$^-$ concentration from the sea surface squared temperature relationship in Table 2 from Chance et al. (2014), the O$_3$ concentration in the lowermost level of the model, and the 10 m wind speed from meteorological fields. The 10 m wind speed used by the parametrization is limited to a minimum of 5 m s$^{-1}$ to prevent unsubstantiated emissions at low wind speeds. Annual average iodine emission fluxes are shown in Fig. 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

<table>
<thead>
<tr>
<th>Species</th>
<th>Emissions Tg yr$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$I</td>
<td>0.26</td>
</tr>
<tr>
<td>CH$_3$I$_2$</td>
<td>0.11</td>
</tr>
<tr>
<td>CH$_3$ICl</td>
<td>0.18</td>
</tr>
<tr>
<td>CH$_3$IBr</td>
<td>0.05</td>
</tr>
<tr>
<td>I$_2$</td>
<td>0.32</td>
</tr>
<tr>
<td>HOI</td>
<td>2.91</td>
</tr>
<tr>
<td>Total</td>
<td>3.83</td>
</tr>
</tbody>
</table>
Figure 1. Annual mean surface fluxes for iodine precursors in the “Br+I” simulation in kg m$^{-2}$ s$^{-1}$.

Table 2. Henry’s law coefficients and molar heats of formation of iodine species. Where Henry’s law constant equals infinity a very large value is used within the model (1 $\times$ 10$^{20}$ M atm$^{-1}$). The INO$_2$ Henry’s law constant is assumed equal to that of BrNO$_3$, from Sander (2015), by analogy. For I$_2$O$_X$ (X = 2, 3, 4) a Henry’s law constant of infinity is assumed by analogy with INO$_3$.

<table>
<thead>
<tr>
<th>Num.</th>
<th>Species</th>
<th>Henry’s law constant</th>
<th>Reference</th>
<th>Molar heat of formation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>HOI</td>
<td>$1.53 \times 10^4$</td>
<td>Sander (2015)</td>
<td>$-8.37 \times 10^3$</td>
<td>Sander et al. (2006)</td>
</tr>
<tr>
<td>D2</td>
<td>HI</td>
<td>$2.35 \times 10^{10}$</td>
<td>Sander (2015)</td>
<td>$-3.19 \times 10^3$</td>
<td>Sander et al. (2006)</td>
</tr>
<tr>
<td>D4</td>
<td>I$_2$O$_2$</td>
<td>$\infty$</td>
<td>see caption text</td>
<td>$-1.89 \times 10^4$</td>
<td>Kaltsoyannis and Plane (2008)</td>
</tr>
<tr>
<td>D5</td>
<td>I$_2$</td>
<td>$2.63 \times 10^0$</td>
<td>Sander (2015)</td>
<td>$-7.51 \times 10^3$</td>
<td>Sander et al. (2006)</td>
</tr>
<tr>
<td>D6</td>
<td>INO$_2$</td>
<td>$3.00 \times 10^{-1}$</td>
<td>see caption text</td>
<td>$-7.24 \times 10^3$</td>
<td>Sander et al. (2006)</td>
</tr>
<tr>
<td>D7</td>
<td>I$_2$O$_3$</td>
<td>$\infty$</td>
<td>see caption text</td>
<td>$-7.70 \times 10^3$</td>
<td>Kaltsoyannis and Plane (2008)</td>
</tr>
<tr>
<td>D8</td>
<td>I$_2$O$_4$</td>
<td>$\infty$</td>
<td>see caption text</td>
<td>$-1.34 \times 10^4$</td>
<td>Kaltsoyannis and Plane (2008)</td>
</tr>
</tbody>
</table>

fluxes calculated in this study are 47% higher than in previous work (Saiz-Lopez et al., 2014), despite using the same parametrization (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 parametrization 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, 2015). This approach is applied to I$_2$, HI, HOI, INO$_2$, INO$_3$, I$_2$O$_2$, I$_2$O$_3$, and I$_2$O$_4$. Aerosol iodine is assumed to have the same wet deposition properties as sulfate aerosol.

Wet deposition is calculated for I$_2$, HI, HOI, INO$_2$, INO$_3$, I$_2$O$_2$, I$_2$O$_3$, and I$_2$O$_4$ 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.

### 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, INO) and processing of higher iodine oxides (I₂O₅, X = 2, 3, 4) after formation of I₂O₅ are not treated explicitly but are parametrized as described in Sect. 2.5.

#### 2.4 Photolysis rates

Photolysis reactions are summarized 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 seven 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 I₂O₅ (X = 2, 3, 4) we assume the same absorption cross-section as INO₅, an approach used previously (Bloss et al., 2010). For most species (I₂, HOI, IO, IO, INO, I₂O₂, CH₂I₂, CH₂IBr, and CH₂ICl) we assume a quantum yield of 1, but for INO₃ we use a quantum yield of 0.21 (Sander et al., 2011).
Table 4. Termolecular iodine reactions. The lower pressure limit rate \((k_0)\) is given by: \(A_0 \cdot \exp\left(\frac{E_a}{RT}\right) \cdot \left(\frac{300}{T}\right)^x\). The high-pressure limit is given by \(k_\infty\). \(F_c\) characterizes 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.

<table>
<thead>
<tr>
<th>Rxn ID</th>
<th>Reaction</th>
<th>(A_0) cm(^6) molecules(^{-2}) s(^{-1})</th>
<th>(E_a/R) K</th>
<th>(x)</th>
<th>(k_\infty) cm(^3) molecules(^{-1}) s(^{-1})</th>
<th>(F_c)</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>(1 + NO + M \rightarrow INO + M)</td>
<td>(1.80 \times 10^{-32})</td>
<td>300</td>
<td>1</td>
<td>(1.70 \times 10^{-11})</td>
<td>0.60</td>
<td>Atkinson et al. (2007)</td>
</tr>
<tr>
<td>T2</td>
<td>(1 + NO_2 + M \rightarrow INO_2 + M)</td>
<td>(3.00 \times 10^{-31})</td>
<td>300</td>
<td>1</td>
<td>(6.60 \times 10^{-11})</td>
<td>0.63</td>
<td>Atkinson et al. (2007)</td>
</tr>
<tr>
<td>T3</td>
<td>(IO + NO_2 + M \rightarrow INO_3 + M)</td>
<td>(7.70 \times 10^{-31})</td>
<td>–</td>
<td>5</td>
<td>(1.60 \times 10^{-11})</td>
<td>0.40</td>
<td>Atkinson et al. (2007)</td>
</tr>
</tbody>
</table>

Table 5. Photolysis reactions of iodine species. For I\(_2\)O\(_X\) \((X = 2, 3, 4)\) the cross-section of INO\(_3\) is used as described in Sect. 2.4.

<table>
<thead>
<tr>
<th>ID</th>
<th>Reaction</th>
<th>Reference cross-section</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>(I_2 + h\nu \rightarrow 2I)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J2</td>
<td>(HOI + h\nu \rightarrow I + OH)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J3</td>
<td>(IO + h\nu \rightarrow I + [O_3])</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J4</td>
<td>(OIO + h\nu \rightarrow I + O_2)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J5</td>
<td>(INO + h\nu \rightarrow I + NO)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J6</td>
<td>(INO_2 + h\nu \rightarrow I + NO_2)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J7</td>
<td>(INO_3 + h\nu \rightarrow I + NO_3)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J8</td>
<td>(I_2O_2 + h\nu \rightarrow I + OIO)</td>
<td>see caption</td>
</tr>
<tr>
<td>J9</td>
<td>(CH_3I + h\nu \rightarrow I + CH_2O_2)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J10</td>
<td>(CH_3I_2 + h\nu \rightarrow 2I + (CH_2))</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J11</td>
<td>(CH_3Cl + h\nu \rightarrow I + (CH_2Cl))</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J12</td>
<td>(CH_3Br + h\nu \rightarrow I + (CH_2Br))</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>J20</td>
<td>(I_2O_3 + h\nu \rightarrow 2IO)</td>
<td>see caption</td>
</tr>
<tr>
<td>J21</td>
<td>(I_2O_3 + h\nu \rightarrow OIO + IO)</td>
<td>see caption</td>
</tr>
</tbody>
</table>

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 1/2I\(_2\) on sea-salt aerosol alone, whereas irreversible loss via uptake of HI leads to the generation of aerosol phase iodine. Uptake of I\(_2\)O\(_X\) \((X = 2, 3, 4)\) 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 \((\gamma)\). Reactions considered and values of \(\gamma\) used are based on recommendations and previous studies (see Table 6 and Sect. A1.2).

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 < \(p\)) \((\sim 2\) pmol mol\(^{-1}\), Read et al., 2008) by a ratio of \(\sim 5\) \((0.4\) pmol mol\(^{-1}\)). 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 (“Br+I”), which includes both iodine and bromine chemistry (Sect. 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).
Figure 2. Annual mean zonal tropospheric mixing ratios for precursor and reactive iodine compounds (pmol mol$^{-1}$) in the simulation with both iodine and bromine chemistry (“Br+I”). No calculations of concentrations are made within the stratosphere and so that region is left blank.

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. Asterisked (*) reactions proceed only on sea-salt aerosols.

<table>
<thead>
<tr>
<th>ID</th>
<th>Reaction</th>
<th>Reactive uptake coefficient ($\gamma$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>HI $\rightarrow$ iodine aerosol</td>
<td>0.10*</td>
<td>Crowley et al. (2010)</td>
</tr>
<tr>
<td>K2</td>
<td>INO$_3$ $\rightarrow$ 0.5I$_2$</td>
<td>0.01*</td>
<td>see caption text</td>
</tr>
<tr>
<td>K3</td>
<td>HOI $\rightarrow$ 0.5I$_2$</td>
<td>0.01*</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>K4</td>
<td>INO$_2$ $\rightarrow$ 0.5I$_2$</td>
<td>0.02*</td>
<td>see caption text</td>
</tr>
<tr>
<td>K5</td>
<td>I$_2$O$_2$ $\rightarrow$ iodine aerosol</td>
<td>0.02</td>
<td>see caption text</td>
</tr>
<tr>
<td>K6</td>
<td>I$_2$O$_4$ $\rightarrow$ iodine aerosol</td>
<td>0.02</td>
<td>see caption text</td>
</tr>
<tr>
<td>K7</td>
<td>I$_2$O$_3$ $\rightarrow$ iodine aerosol</td>
<td>0.02</td>
<td>see caption text</td>
</tr>
</tbody>
</table>

pear to be better simulated in the marine boundary layer (900 hPa < $p$) where measurements are available (Fig. 4). Although not definitive, this brief comparison suggests that 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 data set reported concentrations increasing between dusk and dawn in the range 0.2 to 1.7 pmol mol$^{-1}$ 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$^{-1}$. Some component of this overestimate probably relates to the model’s iodine heterogeneous recycling which assumes 100% conversion of HOI, INO$_3$, and INO$_2$ into 1/2I$_2$ 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. 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 data sets (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
Figure 3. Annual mean surface mixing ratios for precursor and reactive iodine (pmol mol$^{-1}$) 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 Sect. 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 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.

Within ~ 22 and ~ 16% respectively. However, the model overestimates the Malasapina cruise IO concentrations (bias ~ +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 averaged (onto a 20° grid), an average bias of ~ +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 the free troposphere (350 hPa < p < 900 hPa). The median bias in the upper troposphere (350 hPa > 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, data sets, and measurement groups. Increased global coverage, especially vertically, and inter-comparison of observational techniques are needed to better constrain the IO distribution.
Table 7. Comparison between global tropospheric OX budgets of simulations “BROMINE”, “Br+I”, “IODINE”, and “NOHAL” are described here. “BROMINE” includes just bromine chemistry, “Br+I” 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 O3 loss to bromine and half to iodine. Values are rounded to the nearest integer value.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>“NOHAL”</th>
<th>“IODINE”</th>
<th>“BROMINE”</th>
<th>“Br+I”</th>
<th>ACCENT Young et al. (2013)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3 burden (Tg)</td>
<td>390</td>
<td>357</td>
<td>367</td>
<td>334</td>
<td>340±40</td>
</tr>
<tr>
<td>OX chemical sources (Tg yr(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO + HO2</td>
<td>3667</td>
<td>3680</td>
<td>3512</td>
<td>3529</td>
<td>–</td>
</tr>
<tr>
<td>NO + CH3O2</td>
<td>1332</td>
<td>1383</td>
<td>1269</td>
<td>1307</td>
<td>–</td>
</tr>
<tr>
<td>Other OX sources</td>
<td>502</td>
<td>518</td>
<td>505</td>
<td>521</td>
<td>–</td>
</tr>
<tr>
<td>Total chemical OX sources (PO X)</td>
<td>5501</td>
<td>5581</td>
<td>5286</td>
<td>5357</td>
<td>5110±606</td>
</tr>
<tr>
<td>OX chemical sinks (Tg yr(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3 + hν + H2O → 2OH + O2</td>
<td>2579</td>
<td>2271</td>
<td>2425</td>
<td>2119</td>
<td>–</td>
</tr>
<tr>
<td>O3 + HO2 → OH + O2</td>
<td>1391</td>
<td>1186</td>
<td>1274</td>
<td>1080</td>
<td>–</td>
</tr>
<tr>
<td>O3 + OH → HO2 + O2</td>
<td>687</td>
<td>627</td>
<td>621</td>
<td>560</td>
<td>–</td>
</tr>
<tr>
<td>HOB Br + hν → Br + OH</td>
<td>–</td>
<td>–</td>
<td>166</td>
<td>143</td>
<td>–</td>
</tr>
<tr>
<td>HOB Br + HBr → Br2 + H2O (aq. aerosol)</td>
<td>–</td>
<td>–</td>
<td>8</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>BrO + BrO → 2Br + O2</td>
<td>–</td>
<td>–</td>
<td>12</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>BrO + BrO → Br2 + O2</td>
<td>–</td>
<td>–</td>
<td>3</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>BrO + OH → Br + HO2</td>
<td>–</td>
<td>–</td>
<td>6</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>IO + BrO → Br + I + O2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>7</td>
<td>–</td>
</tr>
<tr>
<td>Other bromine OX sinks</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Total bromine OX sinks</td>
<td>–</td>
<td>–</td>
<td>195</td>
<td>178</td>
<td>–</td>
</tr>
<tr>
<td>HOI + hν → I + OH</td>
<td>–</td>
<td>639</td>
<td>–</td>
<td>583</td>
<td>–</td>
</tr>
<tr>
<td>HOI → 0.5I2 (sea-salt aerosol)</td>
<td>–</td>
<td>2</td>
<td>–</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>IO + BrO → Br + I + O2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>7</td>
<td>–</td>
</tr>
<tr>
<td>OIO + hν → I + O2</td>
<td>–</td>
<td>114</td>
<td>–</td>
<td>156</td>
<td>–</td>
</tr>
<tr>
<td>Other iodine OX sinks</td>
<td>–</td>
<td>1</td>
<td>–</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Total iodine OX sinks</td>
<td>–</td>
<td>756</td>
<td>–</td>
<td>748</td>
<td>–</td>
</tr>
<tr>
<td>Other OX sinks</td>
<td>176</td>
<td>181</td>
<td>172</td>
<td>179</td>
<td>–</td>
</tr>
<tr>
<td>Total chem. OX sinks (LO X)</td>
<td>4833</td>
<td>5021</td>
<td>4687</td>
<td>4864</td>
<td>4668±727</td>
</tr>
<tr>
<td>O3 (PO X)-L(O X) (Tg yr(^{-1}))</td>
<td>668</td>
<td>560</td>
<td>599</td>
<td>493</td>
<td>618±251</td>
</tr>
<tr>
<td>O3 Dry deposition (Tg yr(^{-1}))</td>
<td>949</td>
<td>850</td>
<td>886</td>
<td>791</td>
<td>1003±200</td>
</tr>
<tr>
<td>O3 Lifetime (days)</td>
<td>25</td>
<td>22</td>
<td>24</td>
<td>22</td>
<td>22±2</td>
</tr>
<tr>
<td>O3 STE (PO X-LO X-Dry dep.) (Tg yr(^{-1}))</td>
<td>281</td>
<td>290</td>
<td>287</td>
<td>298</td>
<td>552±168</td>
</tr>
</tbody>
</table>

4 Modeled 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 (2I2 + HOI + IO + OIO + HI +INO + INO2 + INO3 + 2I2O2 + 2I2O3 + 2I2O4) 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. 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\(^\circ\)N–60\(^\circ\)S). Most (56 %) of the emissions occur in the Tropics (22\(^\circ\)S to 22\(^\circ\)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\(^{-1}\) (Ordoñez 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
Figure 5. Iodine oxide (IO) surface observations (black) by campaign compared against the simulation with both iodine and bromine chemistry ("Br+I", red). 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 Sect. 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.

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).

Annual mean surface concentrations (Fig. 3) of IO are ubiquitously found over the oceans at \( \sim 0.25–1 \text{ pmol mol}^{-1} \). Minor species (e.g. HI, OIO) are modelled at greatest mixing ratios over the tropical oceans and towards the poles. Iodine compounds are formed through interacts with NO\(_X\) (INO\(_3\)/INO\(_2\)) peaking in the Northern Hemisphere in polluted oceanic regions. However, due to limited or non-existent measurements of these species in the remote marine boundary layer, these species offer limited ability to constrain the modelled values.

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\(_2\)O\(_X\)) (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 > \( p > \) tropopause) this can increase by 2 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 − CH\(_2\)I\(_X\) (where \( X = \text{Cl}, \text{Br}, I \)) and I\(_2\) − are negligible outside of the lowest model levels but the concentrations of others (CH\(_3\)I and HOI) persist further through the column. For CH\(_3\)I this is due to its longer lifetime of \( \sim 4 \) 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 \( \sim 10 \) km 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\(_3\)I. Overall, atmospheric iodine is dominated by three IO\(_Y\) species (HOI, IO, and INO\(_3\)) with HOI representing the greatest fraction (\( \sim 70 \%) \) in the free troposphere (350 hPa < \( p < \) 900 hPa).
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 Sect. 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 IY species, with fluxes (Tg I yr$^{-1}$) shown on arrows. Red lines, photolysis; blue lines, chemical pathways; green lines, emission source; orange lines, heterogeneous pathway; purple lines, depositional 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.

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$^{-1}$, with higher iodine oxides (I$_2$O$_X$ (X = 2, 3, 4)) and di-halogenated organics (CH$_2$IX (X = Cl, Br, I)) grouped.
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\(2\) (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 \(> p > \) tropopause) (up to nine times) and beyond latitudes of 80° N and S (up to four 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 \(> p > \) 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 O\(3\) and OH

O\(3\) and OH are two key parameters for climate and air quality. Previous studies (Bloss et al., 2005b; 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 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% in 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$^{-1}$ 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 and Evans, 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 11. Seasonal cycle of near-surface O$_3$ at a range of Global Atmospheric Watch (GAW) sites (Sofen and Evans, 2015). Observational data shown are a 6-year monthly average (2006–2012). Model data are for 2005. Data are from GAW compile and processed as described in Sofen and Evans (2015). Red indicates standard GEOS-Chem (v9-2) including bromine chemistry (“BROMINE”) and green with inclusion of iodine chemistry (“Br+I”).

5.2 O$_3$ budget

We diagnose the impact of iodine on O$_3$ by calculating the model’s tropospheric odd oxygen (O$_X$) budget in Table 7. Here we define O$_X$ as defined in footnote 1.

Iodine 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 produc-
Figure 12. Comparison between annual modelled \( \text{O}_3 \) 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.

Iodine-induced \( \text{O}_3 \) loss within the marine (land mask applied and between 50°N–50°S) troposphere of \( \sim 540 \text{Tg yr}^{-1} \) is comparable to the previously reported values of Saiz-Lopez et al. (2014) when \( \text{I}_2 \text{O}_X \, (X = 2, 3, 4) \) photolysis is included (\( \sim 500 \text{Tg yr}^{-1} \)).

Figure 13 shows the relative importance of different \( \text{O}_X \) sinks in the vertical. The “classical” \( \text{O}_3 \) loss routes (\( h\nu + \text{H}_2\text{O}, \text{HO}_X \)) 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 \( \text{IO}_X \) and \( \text{BrO}_X \) concentrations lead to increased loss of \( \text{O}_3 \).

Figure 14 shows the zonal variation in the different \( \text{O}_X \) destruction terms (in terms of the \( \text{O}_X \) lifetime). It is evi-
dent 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 NOX 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 < p < 900 hPa) where they can destroy O3.

5.3 Impact on OH

Previous box model studies which investigated the impact of iodine on OH concentration in the Antarctic (Saiz-Lopez et al., 2008), mid-latitude coastal (Bloss et al., 2005a), 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 + hv) due to lower O3 concentrations. However, this is more than compensated for by an increase in the rate of conversion of HO2 to OH by IO. Previous studies using constrained box models (Bloss et al., 2005a; 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 7, the global tropospheric burdens of O3 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 O3 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 and Evans, 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 a percentage to 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
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 percentage change from the “Br+I” simulation described in Sects. 2–5. Figure 17 summarizes the fractional impact of these experiments on the globally averaged vertical distribution of I\textsubscript{y}, O\textsubscript{3}, 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 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 parametrization 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\textsubscript{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\textsubscript{y} leads to the mean global OH decreasing by 0.64 % and global tropospheric O\textsubscript{3} increasing by 5.5 %.

7.2 Heterogeneous uptake and cycling

There are 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 → 1/2I\textsubscript{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 (Sect. A1.2). To explore these uncertainties four simulations were run: (1) with the γ values that lead to I\textsubscript{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 IY species) into I₂, thus reducing the rate of HOI deposition. The global IY 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 26 to 100 % (Fig. 17). Decreasing the heterogeneous cycling (“het. cycle/2”) has the opposite impact of roughly the same magnitude – global average IY 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 these changes is small overall. Increased iodine cycling leads to a decrease in the tropospheric O₃ burden of 0.69 % and global mean OH increases by 0.05 %, whereas decreased cycling leads to the tropospheric O₃ burden increasing by 0.56 % and OH decreasing by 0.09 %.

By removing the release of I₂ to the gas-phase following uptake of iodine (“no het. cycle”) or by considering irreversible iodine loss to sulfate aerosol (“Sulfate uptake”) the global IY 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 IY 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

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 three simulations: (1) absorption cross-sections were doubled (“I₂Oₓ 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 (“I₂Oₓ exp. X-sections”), (3) and finally no I₂Oₙ photolysis at all was considered (“No I₂Oₓ photolysis”).

Sensitivity runs “I₂Oₓ X-sections × 2” and “I₂Oₓ exp. X-sections” increase photolysis rates, therefore resulting in an increase in the IY lifetime of 5.3 and 8.3 % and the IY burdens 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 “I₂Oₓ X-sections × 2” and “I₂Oₓ exp. X-sections” respectively. Both these simulations 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 “I₂Oₓ X-sections × 2” and “I₂Oₓ exp. X-sections” respectively. Global mean OH concentrations increase by 0.05 and 0.09 % respectively.

The removal of I₂Oₙ (X = 2, 3, 4) photolysis reduces the global tropospheric IY 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 I₂Oₙ photolysis (Fig. 17). This was also noted by Prados-Roman et al. (2015b) with respect to surface observations.

Our “No I₂Oₓ photolysis” simulation is akin to the “base” simulation of Saiz-Lopez et al. (2014). This was presented...
as a lower bound for iodine chemistry. Their “JI\textsubscript{X}O\textsubscript{Y}” simulation, is akin to our “Br+I”. Saiz-Lopez et al. (2014) find a decrease in marine tropospheric \textsubscript{O\textsubscript{3}} column burden of 3.0 and 6.1 % compared to a simulation with no iodine chemistry for their “base” and “JI\textsubscript{X}O\textsubscript{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 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) (~2 pmol mol\textsuperscript{-1}) 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\textsuperscript{-1} in the daytime marine boundary layer was run (“MBL BrO 2 pmol mol\textsuperscript{-1}”). Increased BrO leads to increased OIO concentrations (BrO+IO → OIO+Br), which leads to increased higher oxide production which in turn increases I\textsubscript{Y} loss and decreases I\textsubscript{Y} burden (10 %). The median bias in vertical comparisons with TORERO aircraft IO observations decreases by 12 to 71 %. Although the overall tropospheric \textsubscript{O\textsubscript{3}} burden decreases by 3.7 %, the average \textsubscript{O\textsubscript{3}} change at the surface is larger and shows a decrease of 88 % (Fig. 17) which is the largest decrease in \textsubscript{O\textsubscript{3}} found within these sensitivity simulations.

7.5 Ocean surface iodide (I\textsuperscript{−}) concentration

Chance et al. (2014) compiled the available ocean surface iodide (I\textsuperscript{−}) 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 parametrization gave best agreement. Figure 16 shows annual averaged ocean surface iodide generated from both parametrizations. The sea surface temperatures are taken from the annual average 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 differences are apparent in magnitude. The data set 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 parametrization (“Ocean Iodide”) reduces the inorganic iodine flux by 51 % to 1.9 Tg, which in turn decreases the global tropospheric iodine I\textsubscript{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 increases by 0.17% with respect to “Br+I”.

7.6 Higher-oxide lifetime

Within the model we have considered the uptake of the I$_2$O$_X$ (X = 2, 3, 4) to aerosol as an irreversible loss of iodine, with the same reactive probability ($\gamma$) as INO$_2$ (0.02). We assess our sensitivity to this assumption by running simulations doubling (“I$_2$O$_X$ ($\gamma$) × 2”) and halving this value (“I$_2$O$_X$ ($\gamma$)/2”).

The effect of doubling $\gamma$ 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 O$_3$ burden (0.54%), and marginally decrease in global mean OH (0.08%). The effect of halving $\gamma$ 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 O$_3$ burden (0.44%), and marginal increase in OH (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 heterogeneous 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 data sets. 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 deposition is back to the oceans.

Comparisons with the limited IO observational data set 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$_2$O 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 parametrization 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. Different 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.

\[
\text{HOI} + \text{OH} \rightarrow \text{IO} + \text{H}_2\text{O} \quad (M5)
\]

Uncertainties exist over product channels for this reaction (Sommariva et al., 2012). In our study we assume the products are IO and H₂O based on laboratory experiments (Riffault et al., 2005) and previous box model analysis (Sommariva et al., 2012).

\[
\text{INO}_3 + I \rightarrow I_2 + \text{NO}_3 \quad (M12)
\]

This reaction’s rate is based on a single theoretical study (Kaltsøyannis 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).

\[
\text{OIO} + \text{OIO} \rightarrow I_2\text{O}_4 \quad (M17)
\]

This reaction rate is from a single experimental study (Gómez Martín et al., 2007), which yielded a lower limit of 1.2 ± 0.3 × 10⁻¹⁰ cm³ molecules⁻¹ s⁻¹. This reaction is included in this work, along with the reverse reaction (Reaction M24, I₂O₄ → 2OIO).

\[
\text{INO}_3 \xrightarrow{M} \text{IO} + \text{NO}_2 \quad (M26)
\]

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 to a 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 use the most recent theoretical study (Kaltsøyannis and Plane, 2008), which we also use here. The forward reaction (Reaction M25) has been included ubiquitously in iodine modelling work; and the 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.

\[
\text{IO} + \text{OIO} \xrightarrow{M} I_2\text{O}_3 \quad (M21)
\]

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).

\[
I_2\text{O}_2 \xrightarrow{M} \text{IO} + \text{IO} \quad (M22)
\]

\[
I_2\text{O}_2 \xrightarrow{M} \text{OIO} + I \quad (M23)
\]

\[
I_2\text{O}_4 \xrightarrow{M} 2\text{OIO} \quad (M24)
\]

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

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

As described in Sect. 3.1, we stoichiometrically emit I₂ following the 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 (\(\gamma\)) 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 (\(\alpha\)) in the range 0.02 to 0.07 (Sander et al., 2011). 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 \(\gamma\) values used in the 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 parameter by Saiz-Lopez et al. (2007) for which the base case was set as 0.02. A \(\gamma\) value of 0.01 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 \(\gamma\)
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 \( \gamma \) 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 \( \gamma \) values up to 0.1 have also been used (Bloss et al., 2010). In this work \( \gamma \) values of 0.01 and 0.02 are used for INO\(_3\) and INO\(_2\) respectively.

The IUPAC compilation includes a recommendation for HI uptake \( \gamma \) on ice of 0.2 (Crowley et al., 2010), based on three experimental studies. A \( \gamma \) 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 \( \text{I}_2\text{O}_X \) \((X = 2, 3, 4)\) no experimental data are 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 \( \gamma \) value for \( \text{I}_2\text{O}_X \) 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.
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). OX is defined as in footnote 1. CH4 lifetime is calculated globally in the troposphere with respect to loss by reaction with OH.

<table>
<thead>
<tr>
<th></th>
<th>Mean IO MBL surface concentration</th>
<th>Chem. OX loss (LOX)</th>
<th>Chem. OX prod. (POX)</th>
<th>POX -LOX burden deposition</th>
<th>O3</th>
<th>O3</th>
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<td>IOX lifetime</td>
<td>IOY burden</td>
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<td>5.98</td>
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<tr>
<td>Het. cycle (γ)/2</td>
<td>-0.09</td>
<td>0.32</td>
<td>0.41</td>
<td>-3.89</td>
<td>-0.96</td>
<td>-5.04</td>
</tr>
<tr>
<td>No het. cycle</td>
<td>-0.47</td>
<td>2.58</td>
<td>3.07</td>
<td>-61.18</td>
<td>5.38</td>
<td>-46.69</td>
</tr>
<tr>
<td>Sulfate uptake</td>
<td>-0.87</td>
<td>2.70</td>
<td>3.60</td>
<td>-59.60</td>
<td>0.49</td>
<td>-48.49</td>
</tr>
<tr>
<td>Ocean iodide</td>
<td>-0.17</td>
<td>1.22</td>
<td>1.39</td>
<td>16.90</td>
<td>2.77</td>
<td>-23.42</td>
</tr>
<tr>
<td>I2OX X-sections \times 2</td>
<td>0.05</td>
<td>-0.20</td>
<td>-0.25</td>
<td>5.26</td>
<td>0.61</td>
<td>3.10</td>
</tr>
<tr>
<td>I2OX exp. X-sections</td>
<td>0.08</td>
<td>-0.31</td>
<td>-0.39</td>
<td>8.31</td>
<td>0.84</td>
<td>4.81</td>
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<tr>
<td>No I2OX photolysis</td>
<td>-0.90</td>
<td>2.54</td>
<td>3.48</td>
<td>-46.41</td>
<td>-17.68</td>
<td>-34.58</td>
</tr>
<tr>
<td>MBL BrO 2 pmol mol^-1</td>
<td>-3.31</td>
<td>-1.44</td>
<td>1.93</td>
<td>-3.72</td>
<td>3.33</td>
<td>-10.07</td>
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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.

Edited by: M. Uematsu

References


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