We would like to thank the reviewers for their comments which have improved the manuscript. Specific comments from the reviewers are given in bold below, followed by our responses in plain text.

Referee #1

Stone et al. presents a study on the influence of tropospheric halogens on OH and HO_2. The study is based on observations from the Cape Verde Atmospheric Observatory, a chemistry box model, and a global chemical transport model. Overall, the paper is well written and well suited for ACP. I recommend it being accepted following minor revision. I list specific comments and questions below:

1) Line 49: Le Breton et al (2017, doi: 10.1016/j.atmosenv.2017.02.003) have also presented measurements of BrO in the MBL, consider including a citation.

We have included the citation.

2) Line 224: What are the processes behind "Physical loss", is it deposition? If so, I suggest you state this explicitly. Is a lifetime of 24 hour reasonable?

The physical losses incorporate losses such as wet and dry deposition and diffusion out of the box for any model generated species with a sufficiently long lifetime. In our previous work (Stone et al., 2010; Stone et al., 2014) we investigated the sensitivity to the deposition rate, with results indicating that variation of the deposition lifetime between 1 hour and 5 days results in little change to the modelled concentrations of OH and HO_2. We have added the following details to the manuscript for clarification:

Deposition processes, including dry deposition and wet deposition, and diffusion are represented in the model by a first-order loss process, with the first-order rate coefficient equivalent to a lifetime of approximately 24 hours. As discussed by Stone et al. (2010), variation of the deposition lifetime between 1 hour and 5 days results in limited changes to the modelled concentrations of OH and HO_2.

3) Line 244 to 253: The assumption of constant BrO and IO between 9:30 and 18:30 seems overly crude. As can be seen in Figure 3 of Read et al. (reference given in manuscript), it takes approximately 6 hours for BrO and IO to raise from 0 to max. How would the results of the box model study change is more realistic assumptions about the diurnal cycle of BrO and IO are used?

The peak daytime concentrations of BrO and IO are typically reached between 9 am and 10 am, with increases from zero occurring from approximately 6 am, as shown in Figure 3 of Read et al. The discussion in the manuscript is unaffected by the early morning concentrations of BrO and IO owing to the focus on the midday (11 am to 1 pm) concentrations of OH and HO_2, and the HO_2:OH ratio, which are influenced on short timescales. The data presented in Figures 1-3 are potentially affected by the assumption of zero concentrations of BrO and IO before 9:30 am, and we have performed simulations in which concentrations of BrO and IO are set to increase from 6 am until 10 am, at which point the constant concentrations are reached, using the data shown in Figure 3 of Read et al. However, the low concentrations of BrO and IO during this period, and the relatively few data points for OH and HO_2 during these times (there were no measurements of OH or HO_2 at these times of day

during SOS2, as shown in Figures 1 and 3), the data presented in the manuscript are not significantly affected. This is shown in the figure below (Figure S6), combined with the response to referee 2. We propose to combine this figure and to provide the details in the supplementary information to the manuscript.

4) Line 288 to 291: Please specify the additional bromine reactions that were added to the Parella mechanism.

We apologise for the confusion here. The additional bromine reactions are those described by Parella et al. (i.e. in addition to the standard mechanism which does not include any halogen chemistry). We have removed the reference to "additional" in order to clarify this:

Emission rates and bromine chemistry included in the model are described in detail by Parella et al. (2012), with the bromine chemistry scheme described by 19 bimolecular reactions, 2 three-body reactions and 2 heterogeneous reactions using rate coefficients, heterogeneous reaction coefficients and photolysis cross-sections recommended by Sander et al. (2011).

5) Line 477-481: Consider extending the discussion of sea-salt debromination. Schmidt et al (reference given in manuscript) presented two simulations: one without sea salt debromination and one including it. The simulation that included sea salt debromination led to levels of BrO that appeared biased high compared to satellite observations, but reproduce the levels observed in the mid Atlantic MBL (see Figure S8 of Schmidt et al.). How would the result of the global model change is sea salt debromination was included?

We have expanded the discussion of this in the manuscript to include the following details:

The global model simulations reported here predict average mixing ratios of ~0.5 ppt for BrO and ~1 ppt for IO during SOS, and thus underpredict BrO but perform well for IO. The underprediction of BrO at Cape Verde results from recent model updates which exclude emissions of bromine species from sea-salt debromination (Schmidt et al., 2016) in order to provide improved agreement with observations of BrO made by the GOME-2 satellite (Theys et al., 2011) and in the free troposphere and the tropical Eastern Pacific MBL (Gomez Martin et al., 2013; Volkamer et al., 2015; Wang et al., 2015). If sea-salt debromination were included, daytime mixing ratios of BrO at Cape Verde would be approximately 2 ppt, as shown by Parella et al. (2012) and Schmidt et al. (2016), and thus in closer agreement to the observations. Increased modelled concentrations of BrO at Cape Verde resulting from inclusion of sea-salt debromination would have a greater effect on OH and HO_2, leading to more significant decreases in OH and HO_2 when bromine chemistry is included without iodine chemistry, with the larger decrease in OH potentially off-setting the increase in OH observed when bromine and iodine chemistry are combined. However, the current model simulations do not consider the coupling between bromine and sulfur chemistry, which may represent a significant sink for reactive bromine species in the troposphere and balance sources from sea-salt debromination (Chen et al., 2017). These results thus demonstrate the need for further investigation and constraint of sources and emission rates of bromine species, and of the coupling between sulfur chemistry and reactive bromine species. We now discuss the global impacts of halogen chemistry.

Also, consider commenting on the resent study by Chen et al (2017, doi: 10.1002/2017GL073812) that show that sulfur chemistry may provide a missing sink of Bry in the MBL to balance the sea salt debromination source.

We have now included details of this study in our discussion of sea-salt debromination (see above).

Referee #2

The paper presents an interesting comparison between observations of OH and HO_2 at the Cape Verde Observatory and two modelling approaches to evaluate how bromine and iodine chemistry impacts HO_x. The results obtained by the two different model setups are discussed and evaluated in the context of the different chemical schemes and timescales considered in the two models. I found the paper interesting and well structured, presenting results in a clear and complete format and hence I recommend the paper for publication in ACP. Please find below two questions and minor comments for consideration by the authors:

- In page 9, line 244, it is written that the box model is constrained by the mean observed mixing ratio of BrO and IO, 2.5 and 1.4 pptv, respectively. What was the peak value of BrO and IO in the model runs?, if the peak value used was 2.5 and 1.4, did you run a sensitivity with the XO peak values measured by Read et al., 2008 and Mahajan et al., 2010?

The peak values used in the model simulations were 2.5 ppt BrO and 1.4 ppt IO. We have now performed a sensitivity analysis to these mixing ratios, using the upper and lower limits to the diurnal averages reported by Read et al. (3.5 ppt and 1.5 ppt for BrO and 2.0 ppt and 1.0 ppt for IO). The impacts of these changes on the diurnal profiles for OH and HO_2, and on the HO_2:OH ratio, are shown in the figure below (Figure S6). Given the focus of the manuscript on the different trends between the box and global models, rather than the absolute concentrations of BrO and IO, we propose to include this figure (Figure S6), which also includes sensitivity to early morning concentrations of BrO and IO as suggested by reviewer 1, in the supplementary information to the paper for completeness. We have added a comment in the main text (line 248) to refer to the sensitivity to BrO and IO concentrations ("*Sensitivity to these mixing ratios is discussed in the Supplementary Material*") and have added the following details to the Supplementary Material:

Observations of BrO and IO at the Cape Verde Atmospheric Observatory show average diurnal mixing ratios of 2.5 ppt and 1.4 ppt, respectively, which were used as constraints in the box model simulations presented in this work. In order to test the sensitivity of OH and HO_2 to these constraints, we have performed simulations in which the BrO and IO mixing ratios were constrained to the upper and lower limits of the observed values (3.5 ppt and 1.5 ppt for BrO and 2.0 ppt and 1.0 ppt for IO, as reported by Read et al. (2008) and Mahajan et al. (2010)). In addition, simulations were performed in which mixing ratios of BrO and IO increase from 0600 hours and reach the constant values of 2.5 ppt and 1.4 ppt, respectively, as shown by Read et al. (2008). Results from these simulations are shown in Figure S6, and indicate that there are only minor differences in the OH and HO_2 concentrations between simulations performed on constraining to the upper and lower limits of the observed BrO and IO concentrations, and that there is little sensitivity of OH or HO_2 to the early morning mixing ratios of BrO and IO.

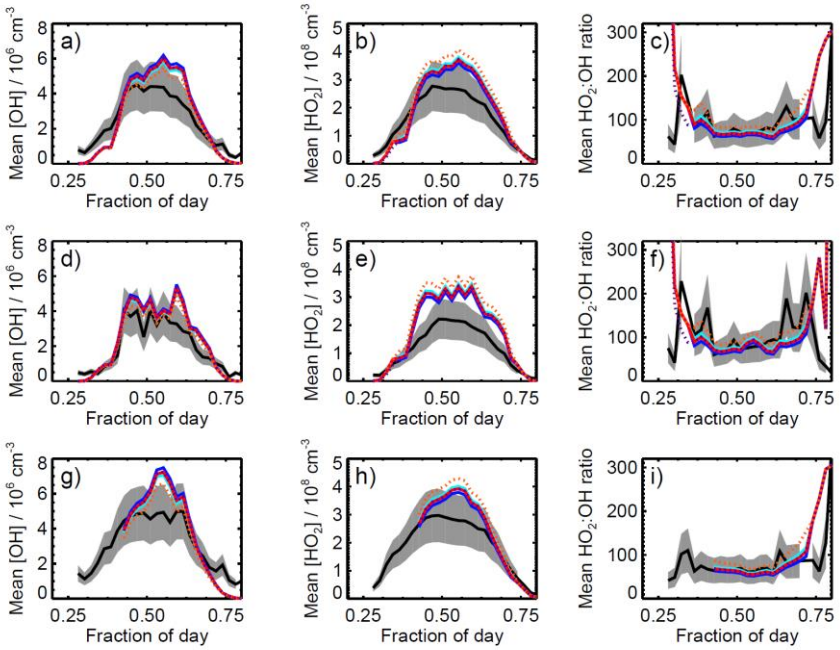

Figure S6: Impacts of changes to BrO and IO constraints on average diurnal profiles for a) OH during both measurement periods; b) HO_2 during both measurement periods; c) HO_2:OH ratio during both measurement periods; d) OH during SOS1 (Feb-Mar 2009); e) HO_2 during SOS1; f) HO_2:OH during SOS1; g) OH during SOS2 (May-June); h) HO_2 during SOS2; i) HO_2:OH ratio during SOS2. Observed data are shown in black, with grey shading indicating the variability in the observations; model simulations constrained to the average daytime (0930 to 1830 hours) mixing ratios of BrO (2.5 ppt) and IO (1.4 ppt) are shown in red; simulations constrained to the upper limits to the daytime mixing ratios of BrO (3.5 ppt) and IO (2.0 ppt) are shown in dark blue; simulations constrained to the lower limits to the daytime mixing ratios of BrO (1.5 ppt) and IO (1.0 ppt) are shown in light blue; simulations constrained to the average daytime mixing ratios of BrO (2.5 ppt) and IO (1.4 ppt) and including increases in the mixing ratios from 0600 hours are shown by the dashed purple lines; simulations with no halogens are shown by the dashed orange lines.

- One thing that I miss in this paper is the how halogen-driven changes in NO_x affect HO_x?. There is not mention to this aspect and from previous modelling studies it is expected to have a bearing on HO_x. I would suggest the authors to mention whether they have explored this coupling and perhaps add some additional results to the revised manuscript.

While we do not explicitly discuss the impacts of halogen-driven changes in NO_x on HO_x, this is included in the model simulations and there are some details in the discussion of the radical budgets and in Figures 4-6 which show how the role of NO_x chemistry in controlling radical budgets changes on inclusion of halogen chemistry. We propose to include the following details to discuss these impacts more thoroughly:

The change in the relative importance of HO_2 + NO on inclusion of halogens in the model results from both the increase in the total HO_2 sink, owing to the additional losses through HO_2 + BrO and HO_2 + IO, and the shift in NO_x partitioning owing to the reactions Br + NO → Br + NO_2 and IO + NO → I + NO_2. The reactions of BrO and IO with NO result in a change in the NO_2:NO ratio of approximately 10 %, on average, which reduces the impact of HO_2 + NO as both a sink for HO_2 and a source for OH.

Minor Comments: P2,L54: " in in HO_x..", please remove one "in".

We have corrected this.

P3,L81: please replace "troposphere" by tropospheric?

We have changed this sentence to:

In general, observationally constrained box model simulations suggest that halogens in the troposphere will increase OH concentrations.

P31,Fig.1: For clarity, please improve quality in the box model results, e.g. what represents the yellow color?

The yellow data points represent the box model concentrations including halogen chemistry. We have corrected the figure caption, which previously stated the points to be orange, and have made some improvements to the presentation of the figure (symbol size, scale) to improve the clarity. Additional plots also are provided in the supplementary material to show these data in more detail

Impacts of bromine and iodine chemistry on tropospheric OH and HO_2: Comparing observations with box and global model perspectives

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Abstract

The chemistry of the halogen species bromine and iodine has a range of impacts on tropospheric composition, and can affect oxidising capacity in a number of ways. However, recent studies disagree on the overall sign of the impacts of halogens on the oxidising capacity of the troposphere. We present simulations of OH and HO_2 radicals for comparison with observations made in the remote tropical ocean boundary layer during the Seasonal Oxidant Study at the Cape Verde Atmospheric Observatory in 2009. We use both a constrained box model, using detailed chemistry derived from the Master Chemical Mechanism (v3.2), and the three-dimensional global chemistry transport model GEOS-Chem. Both model approaches reproduce the diurnal trends in OH and HO_2. Absolute observed concentrations are well reproduced by the box model but are overpredicted by the global model, potentially owing to incomplete consideration of oceanic sourced radical sinks. The two models, however, differ in the impacts of halogen chemistry. In the box model, halogen chemistry acts to increase OH concentrations (by 9.8 % at midday at Cape Verde), while the global model exhibits a small increase in OH at Cape Verde (by 0.6 % at midday) but overall shows a decrease in the global annual mass weighted mean OH of 4.5 %. These differences reflect the variety of timescales through which the halogens impact the chemical system. On short timescales, photolysis of HOBr and HOI, produced by reactions of HO_2 with BrO and IO, respectively, increases the OH concentration. On longer timescales, halogen catalysed ozone destruction cycles lead to lower primary production of OH radicals through ozone photolysis, and thus to lower OH concentrations. The global model includes more of the longer timescale responses than the constrained box model and overall the global impact of the longer timescale response (reduced primary production due to lower O_3 concentrations) overwhelms the shorter timescale response (enhanced cycling from HO_2 to OH), and thus the global OH concentration decreases. The Earth system contains many such responses on a large range of timescales. This work highlights the care that needs to be taken to understand the full impact of any one process on the system as a whole.

Introduction

Halogen chemistry in the troposphere influences budgets of O_3, HO_x (OH and HO_2), NO_x (NO and NO_2) (von Glasow et al., 2004; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015, Schmidt et al., 2016; Sherwen et al., 2016a; Sherwen et al., 2016b), affects the oxidation state of atmospheric mercury (Holmes et al., 2006; Holmes et al., 2010), and impacts aerosol formation (Hoffmann et al., 2001; O'Dowd et al., 2002; McFiggans et al., 2004; McFiggans et al., 2010; Mahajan et al., 2011; Sherwen et al., 2016c).

The production of bromine and iodine atoms in the marine boundary layer (MBL) following emissions of organohalogen compounds and the inorganic compounds I_2 and HOI has been shown to result in considerable destruction of tropospheric ozone (Read et al., 2008), leading to the production of bromine monoxide (BrO) and iodine monoxide (IO) radicals. Observations of BrO and IO radicals within the MBL have demonstrated widespread impacts on atmospheric composition and chemistry (Alicke et al., 1999; Sander et al., 2003; Leser et al., 2003; Saiz-Lopez and Plane, 2004; Saiz-Lopez et al., 2004; Peters et al., 2005; Saiz-Lopez et al., 2006; Whalley et al., 2007; Mahajan et al., 2010a; Commane et al., 2011; Dix et al., 2013; Gomez Martin et al., 2013; Le Breton et al., 2017), including significant effects on HO_x concentrations and on the HO_2:OH ratio in coastal and marine locations (Bloss et al., 2005a; Sommariva et al., 2006; Bloss et al., 2007; Bloss et al., 2010; Kanaya et al., 2007; Whalley et al., 2010).

The role of halogens in HO_x chemistry was demonstrated during the NAMBLEX campaign in Mace Head, Ireland, (Heard et al., 2006), following several studies which attributed box model overestimates of HO_2 observations in marine environments to unmeasured halogen monoxides (Carslaw et al., 1999; Carslaw et al., 2002; Kanaya et al., 2001; Kanaya et al., 2002; Kanaya et al., 2007). Simultaneous measurements of OH and HO_2 by laser-induced fluorescence (LIF) (Bloss et al., 2005a; Smith et al., 2006) and halogen species by a combination of DOAS (for BrO or IO, OIO and I_2) (Saiz-Lopez et al., 2006) and broadband cavity ringdown spectroscopy (BBCRDS) (for OIO and I_2) (Bitter et al., 2005) during NAMBLEX enabled box model calculations to fully explore the impacts of halogens on the local composition. A box model without halogen chemistry was able to reproduce the NAMBLEX OH observations to within 25 %, but HO_2 observations were overestimated by up to a factor of 2 (Sommariva et al., 2006). The introduction of halogen chemistry, using DOAS measurements of BrO and IO (Saiz-Lopez et al., 2006) to constrain the model, increased the modelled OH concentrations by up to 15 % and decreased HO_2 by up to 30 % owing to reactions of HO_2 with XO radicals to form HOX which subsequently photolysed to X + OH (Sommariva et al., 2006). Bloss et al., (2005a) indicated that up to 40 % of the instantaneous HO_2 loss could be attributed to HO_2 + IO, and that photolysis of HOI was responsible for 15 % of the noontime OH production.

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The impacts of halogen chemistry on HO_x radicals at a site representative of the open ocean have been investigated at the Cape Verde Atmospheric Observatory (CVAO). Measurements of halogen monoxides (Mahajan et al., 2010a) at the site have been shown to have significant impacts on local ozone concentrations, notably in the magnitude of the daily cycle (Read et al., 2008), and have been used to constrain box model calculations used to explore observations of OH and HO_2 made during the RHaMBLe campaign in 2007 (Whalley et al., 2010). The model calculations showed generally good comparisons with the observed OH and HO_2 concentrations, apart from a period characterised by unusually high concentrations of HCHO. Compared to a model run in which halogen chemistry was absent, bromine and iodine chemistry led to a 9 % increase in the modelled OH concentration (Whalley et al., 2010). Owing to the dominance of the tropics in global methane oxidation (Bloss et al., 2005b), such an impact of halogens on OH could have significant consequences for estimates of global methane lifetimes, and on our understanding of the impacts of halogen chemistry on climate change.

In general, observationally constrained box model simulations suggest that halogens in the troposphere will increase OH concentrations, primarily because of a change in the HO_2 to OH ratio occurring as a result of reactions of halogen oxides (XO) with HO_2 to produce a hypohalous acid (HOX) which photolyses to give an OH radical and a halogen atom (Kanaya et al., 2002; Bloss et al., 2005a; Kanaya et al., 2007; Sommariva et al., 2006; Sommariva et al., 2007; Whalley et al., 2010). Other impacts on the HO_x photochemical system are observed (impacts from changes to NO_x chemistry etc.) but these are minor and overall the general conclusion is that the halogen chemistry tends to increase the OH concentration and thus the oxidising capacity of the atmosphere.

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However, the observationally constrained studies are typically concerned with processes occurring at the surface, and in a single location. The role of halogen chemistry in the troposphere as a whole is more uncertain, particularly in the free troposphere and on a global scale (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). Inclusion of bromine chemistry in the three-dimensional (3D) chemistry transport model (CTM) MATCH-HPIC resulted in decreases in tropospheric ozone concentrations of ~18 % over widespread areas, with regional decreases of up to 40 % (von Glasow et al., 2004). Increases of more than 20 % were found for OH in the free troposphere, but, globally, changes to OH were dominated by decreases in OH in the tropics owing to a reduction in primary production from O_3 photolysis, leading to a decrease of 1-2 % in the global mean OH concentration (von Glasow et al., 2004).

Significant decreases in tropospheric ozone (up to 30% at high latitude spring) were also reported for the pTOMCAT model on inclusion of bromine chemistry (Yang et al., 2005). The CAM-Chem global chemistry-climate model has shown an approximate 10 % decrease in global mean tropospheric ozone concentration on

incorporation of lower bromine emissions (Saiz-Lopez et al., 2012), while the GEOS-Chem CTM displays a global decrease of 6.5 % (Parrella et al., 2012). The GEOS-Chem model indicated that bromine-catalysed loss of ozone is limited by the rate of production of HOBr, and that HO_2 + BrO is responsible for over 95 % of the global tropospheric HOBr production. While HOBr can act as a source of OH on photolysis, the changes to O_3 and NO_x resulting from the inclusion of bromine chemistry in GEOS-Chem led to a 4 % decrease overall in the global annual mean OH (Parrella et al., 2012).

Vertically resolved airborne measurements of IO radicals in the free troposphere over the Pacific Ocean have also demonstrated a role for iodine chemistry throughout the free troposphere, with IO observed at a mixing ratio of ~0.1 ppt in the free troposphere and found to be present in both recent deep convective outflow and aged free tropospheric air (Dix et al., 2013). Model simulations to investigate iodine-driven ozone destruction throughout the troposphere indicated that only 34 % of the total iodine-driven ozone loss occurs within the marine boundary layer, with 40 % occurring in a transition layer and 26 % in the free troposphere (Dix et al., 2013).

The CAM-Chem and GEOS-Chem models have also been updated to encompass iodine chemistry, with results from CAM-Chem showing iodine chemistry to be responsible for 17-27 % of the ozone loss in the tropical MBL and 11-27 % of the ozone loss in the marine upper troposphere (Saiz-Lopez et al., 2014). The GEOS-Chem model also showed iodine chemistry to be responsible for significant ozone destruction throughout the troposphere (Sherwen et al., 2016a; Sherwen et al., 2016b; Sherwen et al., 2017). The GEOS-Chem simulations, which incorporate chlorine, bromine and iodine chemistry, show a reduction in global tropospheric ozone concentration of 18.6 %, compared to simulations with no halogen chemistry, a reduction in the global mean OH of 8.2 % to a concentration of 1.28×10^6 cm^{-3} and a resulting increase in global methane lifetime of 10.8 % to 8.28 years (Sherwen et al., 2016b).

There is thus a discrepancy between box and global models as to the impact of halogen chemistry on OH concentrations in the troposphere. Box models suggesting that OH radical concentrations should increase and thus that halogens tend to increase the oxidising capacity, whereas the global models tend to suggest the opposite.

In this work, we use both a detailed chemical box model approach and a global chemistry-transport model to investigate the local and global impacts of halogen chemistry on HO_x radical concentrations. We focus on seasonal HO_x observations available from the Cape Verde Atmospheric Observatory (Vaughan et al., 2012). We first provide a summary of the measurement site and the observations, followed by details of the two models used

in this study. We then evaluate the impact of halogens on the concentrations of oxidants in the two modelling frameworks and consider the impact of halogen chemistry on global oxidising capacity.

The Cape Verde Atmospheric Observatory

The Cape Verde Atmospheric Observatory is situated on the north east coast of the island of Sao Vicente (16.848 ^{o}N, 24.871 ^{o}W), approximately 500 km off the west coast of Africa. The observatory is in a region of high marine biological production, and, for 95 % of the time, receives the prevailing northeasterly trade wind directly off the ocean (Read et al., 2008; Carpenter et al., 2010). Measurements at the observatory are considered to be representative of the open ocean, and CO, O_3, VOCs, NO_x and NO_y have been measured near-continuously at the observatory since October 2006 (Lee et al., 2009; Carpenter et al., 2010).

In 2007, the observatory was host to the RHaMBLe intensive field campaign, during which a number of additional measurements were made to complement the long-term measurements at the site (Lee et al., 2010), including LP-DOAS measurements of halogen species (Read et al., 2008; Mahajan et al., 2010a) and formaldehyde (Mahajan et al., 2010b), and LIF-FAGE measurements of OH and HO_2 (Whalley et al., 2010). The halogen monooxide radicals BrO and IO exhibited a 'top-hat' diurnal cycle (Vogt et al., 1999; Vogt et al., 1996; Read et al., 2008; Mahajan et al., 2010a) with essentially zero concentration in the hours of darkness and generally constant values of approximately 2.5 ppt BrO and 1.4 ppt IO during the day.

The RHaMBLe campaign was followed by the Seasonal Oxidants Study (SOS) in 2009, during which measurements of OH and HO_2 were conducted over three periods (Feb-March (SOS1), May-June (SOS2), and September (SOS3)), and are discussed in detail by Vaughan et al. (2012). We present here the results from a modelling study of the HO_x measurements made during SOS1 and SOS2, when supporting measurements are available, using both box and global model approaches. SOS3 is not considered in this work owing to a lack of supporting measurements.

Measurements of OH and HO_2 during the Seasonal Oxidant Study were made by laser-induced fluorescence (LIF) spectroscopy at low pressure using the fluorescence assay by gas expansion (FAGE) technique, and are described in detail by Vaughan et al. (2012). Briefly, ambient air is drawn into a fluorescence cell situated on the roof of a shipping container and maintained at pressures of ~ 2 Torr. The fluorescence cell has two excitation axes, with excess NO added at the second axis to titrate HO_2 to OH, enabling simultaneous detection of OH and HO_2. OH radicals in both excitation axes are excited by laser light at $\lambda \sim 308$ nm, generated by frequency tripling the output

of a solid state Nd:YAG pumped Ti:Sapphire laser system (Bloss et al., 2003). Channel photomultiplier tubes coupled to gated photon counters are used to detect the $A^2\Sigma^+ - X^2\Pi_i$ OH fluorescence signal at $\lambda \sim 308$ nm.

Calibration of the instrument is achieved by measurement of the fluorescence signal from known concentrations of OH and HO_2, produced by the photolysis of water vapour, and was performed over a range of conditions before, during and after the campaign. For OH, the 1 σ limit of detection (LOD) was in the range (2-11) × 10^5 cm^{-3} for a 5 min averaging period, while for HO_2 1 σ LOD was in the range (6-13) × 10^5 cm^{-3} for a 4 min averaging period. Uncertainties (2 σ) in the measurements of OH and HO_2 are ~32 % (Vaughan et al., 2012).

Potential interferences in HO_2 measurements arising from conversion of alkene- and aromatic-derived peroxy radicals to OH within the LIF detection cell, as described by Fuchs et al. (2011), are expected to be small for this work owing to relatively low concentrations of alkenes and aromatics at the Cape Verde observatory (Carpenter et al., 2010; Vaughan et al., 2012). Speciation of the peroxy radicals in the box model output (see Supplementary Material) shows that 87.4 % of the peroxy radicals are HO_2 and CH_3O_2, 6.5 % $CH_3C(O)O_2$ and 1.1 % $C_2H_5O_2$, all of which display no HO_2 interference in the laboratory (Whalley et al., 2013: Stone et al., 2014). Peroxy radicals derived from OH-initiated oxidation of ethene and propene ($HOC_2H_4O_2$ and $HOC_3H_6O_2$, respectively) were found to result in an interference signal for HO_2 in the laboratory (~40 % for the experimental configuration in this work) but each radical comprises only ~0.6 % of the total RO_2 in this work. Thus, model calculations reported here do not include representation of potential HO_2 interferences, although such phenomena may be important in other environments (see for example, Whalley et al., 2013; Stone et al., 2014).

Model Approaches

We interpret the observations using two different modeling frameworks. The first is an observationally constrained box model (DSMACC), the second is a global tropospheric chemistry transport model (GEOS-Chem).

Constrained Box Model

The Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) is described in detail by Emmerson and Evans (2009) and Stone et al. (2010), and is a zero-dimensional model using the Kinetic Pre-Processor (KPP) (Sandu and Sander, 2006). In this work we use a chemistry scheme based on a subsection of the hydrocarbons (ethane, propane, *iso*-butane, *n*-butane, *iso*-pentane, *n*-pentane, hexane, ethene, propene, 1-butene, acetylene, isoprene, toluene, benzene, methanol, acetone, acetaldehyde and DMS) available from the Master Chemical Mechanism version 3.2 (MCM v3.2 http://mcm.leeds.ac.uk/MCM/home.htt) (Jenkin et al., 2003;

Saunders et al., 2003), with a halogen chemistry scheme described by Saiz-Lopez et al. (2006), Whalley et al. (2010) and Edwards et al. (2011). We also include the reaction between OH and CH_3O_2 (Bossolasco et al., 2014; Fittschen et al., 2014; Assaf et al., 2016; Yan et al., 2016), with a rate coefficient of 1.6×10^{-10} cm^3 s^{-1} (Assaf et al., 2016) and products HO_2 + CH_3O (Assaf et al., 2017), the impact of which on the HO_2:OH ratio and CH_3O_2 budget is described in the Supplementary Material. The total number of species in the model is ~1200, with ~5000 reactions. The full chemistry scheme used in the model is given in the Supplementary Data.

All measurements are merged onto a 10 minute timebase for input to the model and the model is run with constraints applied as discussed in our previous work (Stone et al., 2010; Stone et al., 2011; Stone et al., 2014). Concentrations of CH_4 and H_2 are kept constant at values of 1770 ppb (NOAA CMDL flask analysis, ftp://ftp.cmdl.noaa.gov/ccg/ch4/) and 550 ppb (Ehhalt and Rohrer, 2009; Novelli et al., 1999) respectively. Formaldehyde measurements were not available during the SOS and we thus use HCHO concentrations generated by the chemistry in the model, with the modelled HCHO concentrations in broad agreement with previous measurements at the observatory (Mahajan et al., 2010b). Table 1 shows a summary of the input parameters to the model.

Species	Mean	Median	Range
O_3 / ppb	33.8 ± 8.6	30.7	19.6 – 49.7
CO / ppb	102.3 ± 10.3	99.3	87.8 – 127.3
H_2O / ppm	20542.3 ± 2753.8	21290.0	16778.5 – 24909.2
NO / ppt	11.2 ± 10.6	9.0	0.06 – 96.2
Ethane / ppt	961.3 ± 289.4	864.0	625.4 – 1799.2
Propane / ppt	136.1 ± 87.05	111.8	20.2 – 521.5
***iso*-butane / ppt**	13.4 ± 9.8	11.1	0 – 62.7
***n*-butane / ppt**	21.9 ± 17.6	17.8	0 – 112.9
Actylene / ppt	79.0 ± 27.8	70.4	45.0 – 180.5
Isoprene / ppt	0.1 ± 0.4	0	0 – 2.6
***iso*-pentane / ppt**	3.9 ± 3.2	3.3	0 – 22.9
***n*-pentane / ppt**	4.3 ± 3.0	3.9	0 – 21.7
***n*-hexane / ppt**	1.0 ± 0.7	0.9	0 – 4.4
Ethene / ppt	43.6 ± 15.2	46.3	6.4 – 73.2
Propene / ppt	13.5 ± 3.6	13.0	6.2 - 24.1
But-1-ene / ppt	6.5 ± 1.4	6.3	3.5 – 10.6
Benzene / ppt	13.0 ± 17.0	8.3	0 – 64.4
Toluene / ppt	77.9 ± 388.8	0	0 – 2013.9
Acetaldehyde / ppt	511.8 ± 526.0	599.3	0 – 2622.6
Methanol / ppt	247.6 ± 336.2	173.3	0 – 3337.4
DMS / ppt	8.3 ± 38.3	0	0 – 291.8

Table 1: Summary of inputs to the model. Zero values indicate measurements below the limit of detection. Further details can be found in Vaughan et al. (2012) and Carpenter et al. (2010).

Deposition processes, including dry deposition and wet deposition, and diffusion are represented in the model by a first-order loss process, with the first-order rate coefficient equivalent to a lifetime of approximately 24 hours. As discussed by Stone et al. (2010), variation of the deposition lifetime between 1 hour and 5 days results in limited changes to the modelled concentrations of OH and HO_2. Loss of reactive species to aerosol surfaces is represented in the model by parameterisation of a first-order loss process to the aerosol surface (Schwarz, 1986), as discussed by Stone et al. (2014).

A range of aerosol uptake coefficients for HO_2 have been reported in the literature, with recent measurements indicating values of γ_{HO2} between 0.003 and 0.02 on aqueous aerosols (George et al., 2013) while others have reported values of $\gamma_{HO2} \sim 0.1$ (Taketani et al., 2008), and increased uptake coefficients in the presence of Cu and Fe ions (Thornton et al., 2008; Mao et al., 2013). In this work we use a value of $\gamma_{HO2} = 0.1$ in order to maintain consistency with previous modelling studies at the site (Whalley et al., 2010) and to account for potential impacts of ions of copper and iron in aerosol particles influenced by mineral dust (Carpenter et al., 2010; Muller et al., 2010; Fomba et al., 2014; Matthews et al., 2014; Lakey et al., 2015).

The aerosol surface area in the model is constrained to previous measurements of dry aerosol surface area at the observatory, corrected for differences in sampling height between the aerosol and HO_x measurements and for aerosol growth under humid conditions (Allan et al., 2009; Muller et al., 2010; Whalley et al., 2010).

Halogen species are constrained to a 'top-hat' profiles for BrO and IO (Vogt et al., 1999; Vogt et al., 1996; Read et al., 2008), as observed during the RHAMBLE campaign in 2007 (Read et al., 2008; Mahajan et al., 2010a). The observations indicate that while there is day to day variation in BrO and IO concentrations, there is little seasonal variation (Mahajan et al., 2010a). BrO and IO are thus constrained to the mean observed mixing ratios of 2.5 ppt and 1.4 ppt, respectively, for time points between 0930 and 1830 (GMT) and zero for all other times. Sensitivity to these mixing ratios is discussed in the Supplementary Material. In a similar way to NO_x (see Stone et al. (2010; 2011)), concentrations of all bromine or iodine species, including BrO and IO, are permitted to vary according to the photochemistry as the model runs forwards. At the end of each 24 hour period in the model, the calculated concentrations of BrO and IO are compared to the constrained value, and the concentrations of all bromine (Br, Br_2, BrO, HBr, HOBr, $BrONO_2$, $BrNO_2$, BrNO) and iodine (I, I_2, IO, HI, HOI, INO, INO_2, $IONO_2$, OIO, I_2O_2, I_2O_3, I_2O_4, $HOIO_2$) species are fractionally increased or decreased such that the calculated and constrained concentrations of BrO and IO are the same. The model is run forwards in time with diurnally varying photolysis rates until a diurnal steady state is reached, typically requiring between 5 and 10 days.

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Global Model

We use the 3D global chemistry transport model GEOS-Chem (v10-01, www.geos-chem.org). The model has been extensively evaluated against observations (Bey et al., 2001; Evans and Jacob, 2005; Nassar et al., 2009; Mao et al., 2010; Zhang et al., 2010; Parrella et al., 2012; Hu et al., 2017). The model is driven by assimilated winds calculated by the Goddard Earth Observing System at a horizontal resolution of 4° × 5°, with 47 vertical levels from the surface to 50 hPa. Anthropogenic emissions of CO, NO_x and SO_2 are described by the EDGAR 3.2 monthly global inventory (Olivier et al., 2005). Emissions of volatile organic compounds (VOCs) are described by the RETRO monthly global inventory (van het Bolscher, 2008) for anthropogenic sources, with ethane emissions described by Xiao et al., 2008, and the MEGAN v2.1 inventory (Guenther et al., 2006; Barkley et al., 2011) for biogenic sources.

The HO_x-NO_x-VOC-O_3 chemistry scheme in the model is described in detail by Bey et al. (2001) and Mao et al. (2013), with the isoprene oxidation mechanism described by Paulot et al. (2009). Photolysis rates use the FAST-JX scheme (Bian and Prather, 2002; Mao et al., 2010), with acetone photolysis rates updated by Fischer et al. (2012). Stratospheric chemistry is based on LINOZ McLinden et al. (2000) for O_3 and a linearised mechanism for other species as described by Murray et al. (2012).

The model framework includes gas-aerosol partitioning of semi-volatile organic compounds (Liao et al., 2007; Henze et al., 2007; Henze et al., 2009; Fu et al., 2008; Heald et al., 2011; Wang et al., 2011), and heterogeneous chemistry (Jacob, 2000). Coupling between gas phase chemistry and sulfate-ammonium-nitrate aerosol is described by Park et al. (2004) and Pye et al. (2009). A description of dust aerosol in the model is given by Fairlie et al. (2007). Treatment of sea salt aerosol is described by Jaegle et al. (2011). The uptake coefficient for N_2O_5 uses the parameterisation by Evans and Jacob (2005), while that for HO_2 uses the parameterisation of Thornton et al. (2008). A full description of the organic aerosol chemistry in the model is given by Heald et al. (2011).

The model includes recent updates to the chemistry scheme to include bromine chemistry (Parella et al., 2012; Schmidt et al., 2016) and iodine chemistry (Sherwen et al., 2016a; Sherwen et al., 2016b). Sources of tropospheric bromine in the model include emissions of $CHBr_3$, CH_2Br_2 and CH_3Br, and transport of reactive bromine from the stratosphere. Debromination of sea-salt aerosol is not included in the model following the work of Schmidt et al. (2016), which showed better agreement with observations of BrO made by the GOME-2 satellite (Theys et al., 2011) and in the free troposphere and the tropical Eastern Pacific MBL (Gomez Martin et al., 2013; Volkamer et al., 2015; Wang et al., 2015). Emission rates and bromine chemistry included in the model are described in detail by Parella et al. (2012), with the bromine chemistry scheme described by 19 bimolecular reactions, 2 three-body

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reactions and 2 heterogeneous reactions using rate coefficients, heterogeneous reaction coefficients and photolysis cross-sections recommended by Sander et al. (2011).

Iodine sources include emissions of CH_3I, CH_2I_2, CH_2ICl, CH_2IBr, I_2 and HOI. Emissions for CH_3I follow Bell et al. (2002), while those of other organic iodine species use parameterisations based on chlorophyll-a in the Tropics and constant oceanic and coastal fluxes in extratropical regions (Ordonez et al., 2012). Emissions of inorganic iodine species (HOI and I_2) use the results of Carpenter et al. (2013), with oceanic iodide concentrations parameterised by MacDonald et al. (2014). The iodine chemistry scheme includes 26 unimolecular and bimolecular reactions, 3 three-body reactions, 21 photolysis reactions and 7 heterogeneous reactions, using recommendations by Atkinson et al. (2007) and Sander et al. (2011) where available. Full details are given by Sherwen et al. (2016a; 2016b).

Photolysis rates of bromine and iodine compounds are calculated using the FAST-J radiative transfer model (Wild et al., 2000; Bian and Prather, 2002; Mao et al., 2010). Wet and dry deposition are determined as for the standard GEOS-Chem model (Liu et al., 2001; Wesely, 1989; Wang et al., 1998; Amos et al., 2012).

The tropospheric chemistry scheme is integrated using the SMVGEAR solver (Jacobson and Turco, 1994; Bey et al., 2001). The model, provides hourly output at the site of the Cape Verde Atmospheric Observatory. Model simulations have been performed in the absence of halogens, with bromine chemistry, with iodine chemistry and with bromine and iodine chemistry combined. Each model simulation is run for two years, with the analysis performed on the second year (2009) and the first year discarded as model spin-up to enable evolution of long-lived species.

Model Results

We now investigate the impact of halogen chemistry on tropospheric oxidation at Cape Verde within our two modelling approaches.

Constrained Box Model

Figure 1 shows the observed and modelled time series for OH and HO_2 during SOS1 (February, March 2009) and SOS2 (May, June 2009). Observed concentrations of OH and HO_2 were typically higher in SOS2 than SOS1, reaching maximum values in SOS2 of ~ 9×10^6 cm^{-3} OH and 4×10^8 cm^{-3} HO_2 (Vaughan et al., 2012). Similar concentrations were observed in May and June 2007 during the RHaMBLe campaign (Whalley et al., 2010), with a *t*-test indicating no statistically significant difference between the OH concentrations measured in May-June

2009 to those measured in May-June 2007 at the 95 % confidence level (Vaughan et al., 2012). Concentrations of HO_2 measured in May-June 2009 were significantly higher than those measured in May-June 2007 at the 95 % confidence level, but were within the 1σ day-to-day variability (Vaughan et al., 2012). Temperatures during SOS2 were typically higher than those during SOS1, with higher relative humidity during SOS2 (Vaughan et al., 2012). Air masses during SOS1 had strong contributions from Atlantic marine air and African coastal region, with polluted marine air and Saharan dust contributing ~ 20 % and 10 %, respectively, for the first half of the measurement period. Conditions during SOS2 were typically cleaner, with Atlantic marine air representing the major source, although coastal African air contributed ~ 40 % on some days. There was little influence from polluted air, dust or continental air (Vaughan et al., 2012). Analysis of the variance of OH and HO_2 during SOS indicated that ~70 % of the total variance could be explained by diurnal behaviour, with the remaining ~30 % related to changes in air mass.

Figure 1 shows the observed and modelled time series for OH and HO_2, for model simulations with and without halogen chemistry. For SOS1, the box model overpredicts the OH and HO_2 concentrations at the start of the campaign (Julian days 59 and 61), but performs better for day 63, and captures both the observed diurnal profile and the observed concentrations. For SOS2, the box model tends to agree better with the observations for both OH and HO_2. A day-by-day comparison between the models and the observations is shown in the Supplementary Material for days for which box model calculations were possible, which were limited by the availability of supporting data.

Figure 2 shows the point-by-point model performance for OH and HO_2 for all data points combined, and for SOS1 and SOS2 separately, for the full box model run including halogen chemistry. There is a tendency for overprediction of OH and HO_2 during SOS1 (slopes of modelled vs observed concentrations are (1.86 ± 0.26) for OH and (1.66 ± 0.21) for HO_2), which is dominated by the model overpredictions on days 59 and 61, with better agreement observed during SOS2 (slopes of modelled vs observed concentrations are (1.11 ± 0.15) for OH and (1.21 ± 0.12) for HO_2).

The measured and modelled average diurnal profiles of OH, HO_2 and the HO_2 to OH ratios are shown in Figure 3. At midday (1100-1300), the full model including halogen chemistry overpredicts OH by a median factor of 1.52 and HO_2 by a median factor of 1.21. A model run containing bromine chemistry but no iodine chemistry gave median midday overpredictions of 1.40 and 1.30 for OH and HO_2, respectively, while a run containing iodine but not bromine gave equivalent median overpredictions of 1.50 and 1.26, respectively. With no halogen chemistry included in the model, the modelled OH decreases, giving a median overprediction at midday by a

factor of 1.37, while the modelled HO_2 increases, resulting in a median overprediction by a factor of 1.37 at midday.

Thus the inclusion of halogens (bromine and iodine) in the box model changes the mean noon time OH and HO_2 concentrations by +9.8 % and –9.9 %, respectively. This impact of halogen chemistry is consistent in sign and magnitude with previous studies (Kanaya et al., 2002; Bloss et al., 2005a; Kanaya et al., 2007; Sommariva et al., 2006; Sommariva et al., 2007; Whalley et al., 2010).

Figure 4 shows the mean midday total RO_x budget (given the fast processing time between HO_2 and HOBr/HOI we identify the RO_x family as OH, HO_2, HOBr, HOI, RO and RO_2) for the two measurement periods during SOS for model runs with and without halogens. These budgets are similar both between time periods (i.e. SOS1 vs SOS2) and for box model calculations with and without halogen chemistry. Radical production dominated by photolysis of ozone (~83 %), with photolysis of HCHO (~10 %), CH_3CHO (~2 %) and H_2O_2 (~2 %) playing a significantly smaller role. Radical termination reactions were dominated by $HO_2 + CH_3O_2$ (~23 %), aerosol uptake of HO_2 (~21 %), $HO_2 + HO_2$ (~19 %), $CH_3C(O)O_2 + HO_2$ (~8 %), and $OH + HO_2$ (~5 %). The inclusion of the reaction between OH and CH_3O_2 reduces the importance of radical termination via $HO_2 + CH_3O_2$ (from ~26 % of the total to ~23 % of the total), but otherwise has little impact on the total radical removal owing to the expected production of $HO_2 + CH_3O$ (Assaf et al., 2017). Further details regarding the impact of the reaction between OH and CH_3O_2 on the HO_2:OH ratio and CH_3O_2 budget are given in the Supplementary Material.

The budget analyses for SOS are consistent with those determined for the RHaMBLe campaign (Whalley et al., 2010; Fittschen et al., 2014; Assaf et al., 2017), reflecting similarities in observed concentrations of long-lived species and the method of the model constraint with observed O_3 concentrations and photolysis rates. The primary source of radicals therefore remains fixed in all simulations, with the primary sinks for these species occurring through radical-radical reactions. Thus, the total radical concentration and budget is little impacted by the presence of halogens.

However, the partitioning of the radicals is impacted by the halogens. Without halogens the average midday (1100-1300) HO_2 to OH ratio is (83.4 ± 15.4) (median = 82.7), with the halogens this changes to (68.3 ± 13.6) (median = 66.9) (Table 2). This change in partitioning is mainly due to the reaction of HO_2 with BrO and IO followed by the photolysis of HOBr and HOI to give OH. In this way the halogens tend to reduce the concentration of HO_2 and increase the concentration of OH.

	HO_2:OH ratio
Observed	79.1 ± 34.1 (70.7)
Box model, no halogens	83.4 ± 15.4 (82.7)
Box model with Br chemistry	78.9 ± 15.6 (77.8)
Box model with I chemistry	71.5 ± 13.0 (70.4)
Box model with Br and I chemistry	68.3 ± 13.6 (66.9)
Global model, no halogens	80.8 ± 18.1 (78.9)
Global model with Br chemistry	81.9 ± 19.0 (79.7)
Global model with I chemistry	70.4 ± 12.5 (70.5)
Global model with Br and I chemistry	71.3 ± 13.2 (71.3)

Table 2: Mean (± 1σ) midday (1100-1300 hours) ratios of HO_2 to OH (SOS1 and SOS2 combined). Median values are given in parentheses.

In the box model without halogen chemistry, production of OH is dominated by ozone photolysis (76 %), HO_2 + NO (12 %) and HO_2 + O_3 (9 %), with OH loss controlled by OH + CO (37 %), OH + CH_4 (16 %) and OH + CH_3CHO (15 %), as shown in Figure 5. Production of HO_2 in the model excluding halogens is controlled by OH + CO (45 %), CH_3O + O_2 (19 %) and photolysis of HCHO (10 %), with loss governed by aerosol uptake (26 %), HO_2 + HO_2 (26 %), HO_2 + NO (15 %), HO_2 + CH_3O_2 (12 %) and HO_2 + O_3 (10 %). In the presence of halogens, the instantaneous budgets for OH and HO_2 are impacted by BrO and IO, as shown in Figures 5 and 6. For the model run including halogens, OH production is still dominated by ozone photolysis (68 %), but there are significant contributions from photolysis of HOI (10 %) and HOBr (3 %). Loss of HO_2 is also affected by the presence of the halogen species, with the dominant loss processes including aerosol uptake (20 %), HO_2 + HO_2 (19 %), HO_2 + IO (14 %), HO_2 + NO (12 %), HO_2 + CH_3O_2 (11 %), HO_2 + O_3 (8 %) and HO_2 + BrO (6 %). The change in the relative importance of HO_2 + NO on inclusion of halogens in the model results from both the increase in the total HO_2 sink, owing to the additional losses through HO_2 + BrO and HO_2 + IO, and the shift in NO_x partitioning owing to the reactions Br + NO → Br + NO_2 and IO + NO → I + NO_2. The reactions of BrO and IO with NO result in a change in the NO_2:NO ratio of approximately 10 %, on average, which reduces the impact of HO_2 + NO as both a sink for HO_2 and a source for OH. As shown in Figures 4-6 there is little difference in the radical budgets between SOS1 and SOS2.

This box modelling study is consistent with previous studies (Kanaya et al., 2002; Bloss et al., 2005a; Kanaya et al., 2007; Sommariva et al., 2007; Whalley et al., 2010; Mahajan et al., 2010a; Stone et al., 2012) in that it implies that halogen chemistry is likely to increase the OH concentration of the marine boundary layer (and potentially

595 other regions of the troposphere) as it enhances the HO_2 to OH conversion through the production of HOBr and
596 HOI. We now look at the impact of halogen chemistry on the concentrations of OH and HO_2 at Cape Verde within
597 the framework of a global atmospheric chemistry model.
598
599 **Global Model**
600 Figure 1 shows the time series for OH and HO_2 calculated by the global model GEOS-Chem, with the average
601 diurnal profiles shown in Figure 3. The global model displays a significant overprediction for OH and HO_2 during
602 SOS1, but exhibits reasonable skill at reproducing the observed concentrations during SOS2 and captures the
603 HO_2:OH ratio for both measurement periods. The overpredictions of OH and HO_2 in the global model likely result
604 from a combination of missing OH-sinks, particularly oxygenated volatile organic compounds (oVOCs) which
605 are currently underestimated in the global model (Millet et al., 2015), and potential overprediction of the primary
606 radical production rate owing to reductions in photolysis rates resulting from cloud cover that are not captured by
607 the global model.
608
609 At midday (1100-1300), the modelled to observed ratios for OH and HO_2 for the global model excluding halogen
610 chemistry are (1.52 ± 1.02) and (1.72 ± 0.80), respectively, with a mean modelled HO_2 to OH ratio of (80.8 ±
611 18.1) (compared to the observed HO_2 to OH ratio of (79.1 ± 34.1)). For the global model run including bromine
612 chemistry, but not iodine, the mean midday modelled to observed ratios for OH and HO_2 are (1.48 ± 1.05) and
613 (1.69 ± 0.81), respectively, with a mean midday modelled HO_2 to OH ratio of (81.9 ± 19.0). Bromine chemistry
614 thus acts to decrease the concentrations of both OH and HO_2, in contrast to the box model results which show
615 increased concentrations of OH and decreased concentrations of HO_2. For the model run including iodine, but not
616 bromine, the midday modelled to observed ratios for OH and HO_2 are (1.57 ± 1.00) and (1.59 ± 0.81), respectively,
617 with a mean midday modelled HO_2 to OH ratio of (70.4 ± 12.5). Iodine chemistry thus results in increased OH
618 and decreased HO_2 for both the global and box model simulations at Cape Verde. Inclusion of bromine and iodine
619 chemistry combined leads to midday modelled to observed ratios of (1.53 ± 1.01) for OH and (1.57 ± 0.82) for
620 HO_2, and a mean midday modelled HO_2 to OH ratio of (71.3 ± 13.2). These results are shown in Table 2, alongside
621 those for the box model.
622
623 The results from the global model at Cape Verde thus differ from those of the box model. For the box model,
624 inclusion of bromine and iodine chemistry, whether separately or combined, leads to increased OH and decreased
625 HO_2 through increased conversion of HO_2 to OH through the production and subsequent photolysis of HOBr and
626 HOI. In the global model a more complex pattern emerges. In a similar way to the box model, the HO_2
627 concentrations in the global model are decreased on inclusion of bromine and/or iodine owing to the additional

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loss reactions HO_2 + BrO and HO_2 + IO. When bromine chemistry is considered in the global model in isolation from iodine chemistry, the OH concentration decreases, despite the production and photolysis of HOBr. This decrease occurs as a result of a reduction in the O_3 concentration in the model on inclusion of bromine chemistry owing to the reaction of Br with O_3, which leads to a decrease in the rate of primary radical production from O_3 photolysis and thus lower OH concentrations. The impact of the decreased radical production rate is greater than that leading to increased OH production through HOBr photolysis, and the net OH concentration is reduced in the global model. This effect is not observed in the box model calculations as the model runs are constrained to long-lived species – including O_3. The change in O_3 concentration on the inclusion of halogen chemistry is thus not considered in the box model simulations, and the subsequent impacts of halogens consider only those changes occurring on a more rapid timescale, which lead to increases in the OH concentration.

However, the inclusion of iodine chemistry in the global model does lead to increased OH concentrations at Cape Verde. Direct emissions of HOI in the global model, in addition to chemical production through HO_2 + IO, result in increased OH production through HOI photolysis as well as the repartitioning of HO_2 and OH through HOI production in a similar manner to that for HOBr. However, the more rapid cycling of HO_2 to OH through the more rapid production and photolysis of HOI compared to HOBr, reduces the impact of iodine chemistry on the HO_2:OH ratio compared to that for bromine chemistry. Iodine chemistry thus can reduce the OH concentration similarly to bromine chemistry, through the destruction of O_3 and subsequent reduction in primary production rate, but the impact is less than that for bromine, and can be offset by the direct emissions of HOI which increases the production rate of OH through photolysis.

The impacts of iodine chemistry in the global model are thus more complex than those for bromine chemistry. When bromine and iodine chemistry are combined in the global model there is a competition between the effects of the reduction in primary production of OH, through depletion of O_3, and the production of OH from photolysis of HOBr and HOI and, for the model simulations at Cape Verde, the impacts of direct HOI emissions dominate. The OH concentration is thus marginally increased compared to simulations containing no halogens, although the HO_2 concentrations are significantly decreased.

The impacts of halogens on OH radical concentrations in the global model thus display a complexity that is somewhat obscured in the box model simulations. Overall, the inclusion of halogens in the global model leads to a slight increase in OH at Cape Verde, but, owing to the opposing effects of bromine and iodine, this result is subject to the modelled concentrations of bromine and iodine species. Observations at Cape Verde made between November 2006 and June 2007 indicate ‘top-hat’ profiles for BrO and IO, with average daytime mixing ratios of

2.5 ppt and 1.4 ppt, respectively, and little variability over the entire campaign (Read et al., 2008; Mahajan et al., 2010a). The global model simulations reported here predict average mixing ratios of ~0.5 ppt for BrO and ~1 ppt for IO during SOS, and thus underpredict BrO but perform well for IO. The underprediction of BrO at Cape Verde results from recent model updates which exclude emissions of bromine species from sea-salt debromination (Schmidt et al., 2016) in order to provide improved agreement with observations of BrO made by the GOME-2 satellite (Theys et al., 2011) and in the free troposphere and the tropical Eastern Pacific MBL (Gomez Martin et al., 2013; Volkamer et al., 2015; Wang et al., 2015). If sea-salt debromination were included, daytime mixing ratios of BrO at Cape Verde would be approximately 2 ppt, as shown by Parella et al. (2012) and Schmidt et al. (2016), and thus in closer agreement to the observations. Increased modelled concentrations of BrO at Cape Verde resulting from inclusion of sea-salt debromination would have a greater effect on OH and HO_2, leading to more significant decreases in OH and HO_2 when bromine chemistry is included without iodine chemistry, with the larger decrease in OH potentially off-setting the increase in OH observed when bromine and iodine chemistry are combined. However, the current model simulations do not consider the coupling between bromine and sulfur chemistry, which may represent a significant sink for reactive bromine species in the troposphere and balance sources from sea-salt debromination (Chen et al., 2017). These results thus demonstrate the need for further investigation and constraint of sources and emission rates of bromine species, and of the coupling between sulfur chemistry and reactive bromine species. We now discuss the global impacts of halogen chemistry.

Deleted: The global model simulations reported here predict average mixing ratios of ~0.5 ppt for BrO and ~1 ppt for IO during SOS, and thus underpredict BrO but perform well for IO. The underprediction of BrO at Cape Verde results from recent model updates which exclude emissions of bromine species from sea-salt debromination (Schmidt et al., 2016) in order to provide improved agreement with observations of BrO made by the GOME-2 satellite (Theys et al., 2011) and in the free troposphere and the tropical Eastern Pacific MBL (Gomez Martin et al., 2013; Volkamer et al., 2015; Wang et al., 2015). We now discuss the global impacts of halogen chemistry.

Global impacts of halogen chemistry on OH and HO_2

On the global scale, concentrations of OH and HO_2 are reduced on inclusion of bromine and iodine chemistry, both individually and combined. The global mass weighted annual mean OH concentration decreases by 3.8 % on inclusion of bromine chemistry, but only 0.02 % on inclusion of iodine chemistry alone. When the chemistry of bromine and iodine is combined in the model, the global mass weighted annual mean OH concentration decreases by 4.5 %. For HO_2, the global mass weighted annual mean is decreased by 4.2 % by bromine, 5.6 % by iodine and 9.7 % by bromine and iodine combined. Figure 7 shows the probability distribution functions for the changes to OH and HO_2 concentrations for the monthly mean values for all grid boxes within the troposphere for the year. For the majority of grid boxes, concentrations of OH and HO_2 are reduced on inclusion of bromine chemistry, with iodine also generally reducing HO_2 concentrations but leading to a wider spread of changes to the OH concentration, and similar numbers of grid boxes showing increased and decreased concentrations. When bromine and iodine chemistry are combined in the model, HO_2 shows a more significant decrease than for either halogen individually, and OH, although exhibiting increased concentrations in a significant number of grid boxes, displays a greater tendency for decreased concentrations.

Figure 8 shows the changes to the annual modelled surface layer OH and HO_2 concentrations on inclusion of halogen chemistry, with annual surface layer mixing ratios of BrO and IO shown in Figure 9. The most significant changes to OH and HO_2 occur over marine regions, particularly over the Southern Pacific. Smaller changes are observed over land, and any increased concentrations, including those for OH over Cape Verde, can be seen to occur in coastal regions where the impacts of direct HOI emissions dominate and concentrations of IO concentrations are typically elevated.

Thus, overall, halogens act to reduce the oxidising capacity of the troposphere through reductions to O_3 and subsequent reductions in the primary production rates of OH and HO_2, despite the slight increase in OH concentration predicted by the global model at Cape Verde. Consideration of the full extent of the impacts of halogens on the global oxidising capacity is hindered by uncertainties in the concentrations and distributions of halogen species, and model representations of halogen processes, particularly those relating to sea salt debromination, ocean iodide emissions, parameterisations of iodine recycling in aerosols and photolysis of higher iodine oxides (Sherwen et al., 2016a).

Conclusions

Measurements of OH and HO_2 made by LIF-FAGE at the Cape Verde Atmospheric Observatory during the Seasonal Oxidants Study in 2009 have been simulated by a constrained box model and a three-dimensional global chemistry transport model. The observations are generally reproduced well by the box model, but are overpredicted by the global model.

The oxidising capacity of the two models, as manifested by the OH concentration, shows opposing sensitivity to halogens. The constrained box model shows an increase in OH concentrations with the inclusion of halogens, whereas the global transport model shows a decrease in OH concentrations globally, despite a marginal decrease in the OH concentration at Cape Verde. This difference between models reflects differing representation of chemical timescales by the models. The box model is constrained to concentrations of long-lived compounds, including O_3, and considers only impacts on short timescales, whereas the global model includes impacts occurring on longer timescales. Within this context, the box model includes the short timescale impact of halogens on the repartitioning of HO_2 to OH, thus increasing OH and decreasing HO_2, but does not consider the longer timescale impact of halogen-mediated ozone destruction which impacts primary radical production. This highlights a general problem with understanding the complex interactions within atmospheric chemistry and the Earth system in general. Evaluating the impact of a small part of the system on the system as a whole can be

difficult and the most significant processes may occur on timescales significantly longer than those of the perturbation.

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Figures

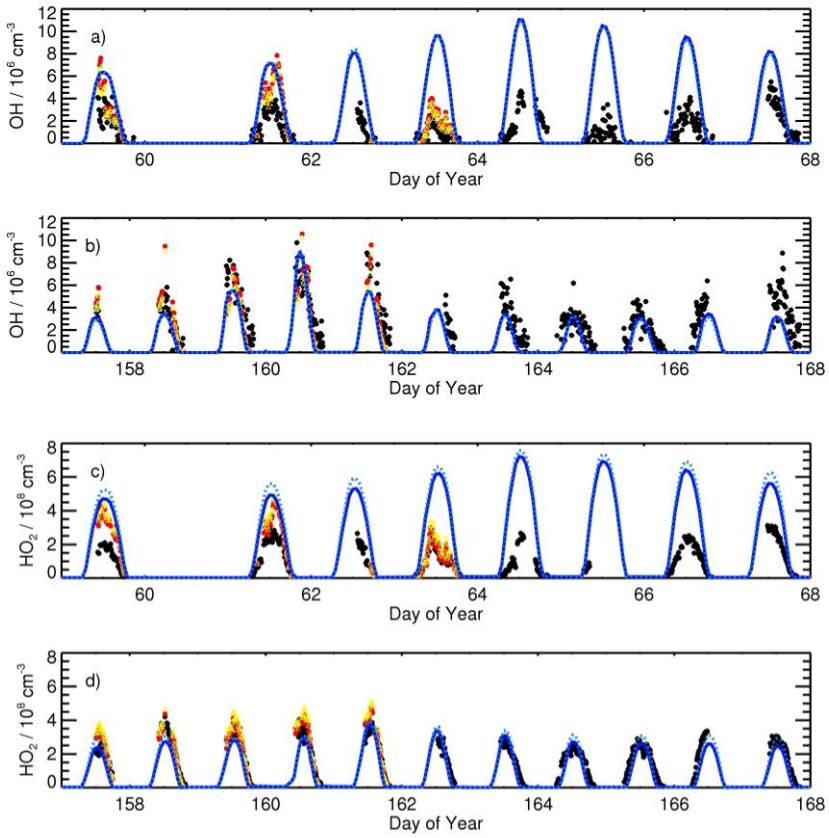

Figure 1: Observed and modelled concentrations of a) OH during SOS1 (February-March 2009, days 58-68); b) OH during SOS2 (May-June 2009, days 157-168); c) HO_2 during SOS1; d) HO_2 during SOS2. Observed data are shown in black; box model concentrations with halogen chemistry are shown by filled red circles; box model concentrations without halogen chemistry are shown by open yellow triangles; global model concentrations with halogen chemistry are shown by solid dark blue lines; global model concentrations without halogen chemistry are shown by broken blue lines.

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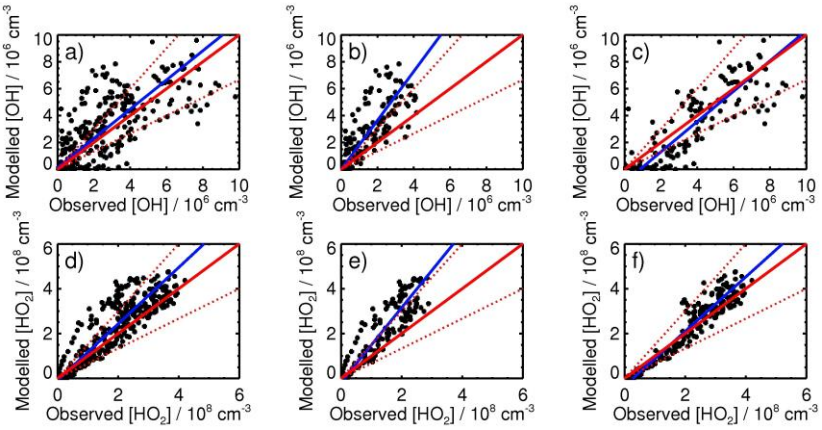

Figure 2: Comparison of modelled and observed concentrations of a) OH during SOS1 (February-March 2009) and SOS2 (May-June 2009); b) OH during SOS1; c) OH during SOS2; d) HO_2 during SOS1 and SOS2; e) HO_2 during SOS1; f) HO_2 during SOS2. In each plot, the solid red line indicates the 1:1 line, with 50 % limits given by the broken red lines. The best fit lines are shown in blue and are described by a) $[OH]_{mod} = (1.09 \pm 0.11) \times [OH]_{obs} + (0.13 \pm 0.38) \times 10^6$ ($r^2 = 0.49$); b) $[OH]_{mod} = (1.82 \pm 0.26) \times [OH]_{obs} - (0.01 \pm 0.51) \times 10^6$ ($r^2 = 0.56$); c) $[OH]_{mod} = (1.11 \pm 0.15) \times [OH]_{obs} - (0.95 \pm 0.66) \times 10^6$ ($r^2 = 0.64$); d) $[HO_2]_{mod} = (1.26 \pm 0.10) \times [HO_2]_{obs} - (0.08 \pm 0.22) \times 10^8$ ($r^2 = 0.77$); e) $[HO_2]_{mod} = (1.66 \pm 0.21) \times [HO_2]_{obs} - (0.17 \pm 0.34) \times 10^8$ ($r^2 = 0.78$); f) $[HO_2]_{mod} = (1.21 \pm 0.12) \times [HO_2]_{obs} - (0.32 \pm 0.30) \times 10^8$ ($r^2 = 0.91$).

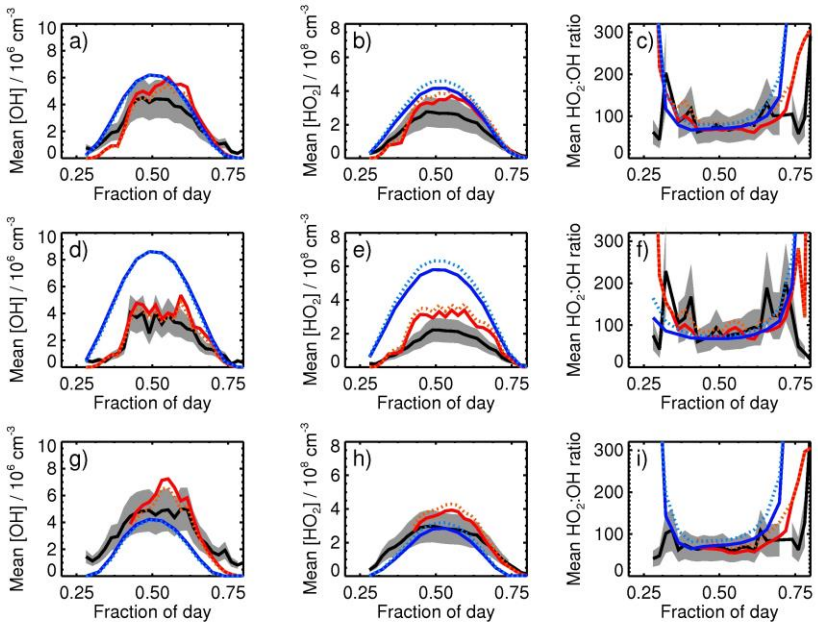

Figure 3: Average diurnal profiles during the Seasonal Oxidant Study (SOS) at the Cape Verde Atmospheric Observatory for a) OH during both measurement periods; b) HO_2 during both measurement periods; c) HO_2:OH ratio during both measurement periods; d) OH during SOS1 (Feb-Mar 2009); e) HO_2 during SOS1; f) HO_2:OH during SOS1; g) OH during SOS2 (May-June); h) HO_2 during SOS2; i) HO_2:OH ratio during SOS2. Observed data are shown in black, with grey shading indicating the variability in the observations; box model output with halogen chemistry is shown by solid red lines; box model output without halogen chemistry is shown by broken orange lines; global model output with halogen chemistry is shown by solid dark blue lines; global model output without halogen chemistry is shown by broken blue lines.

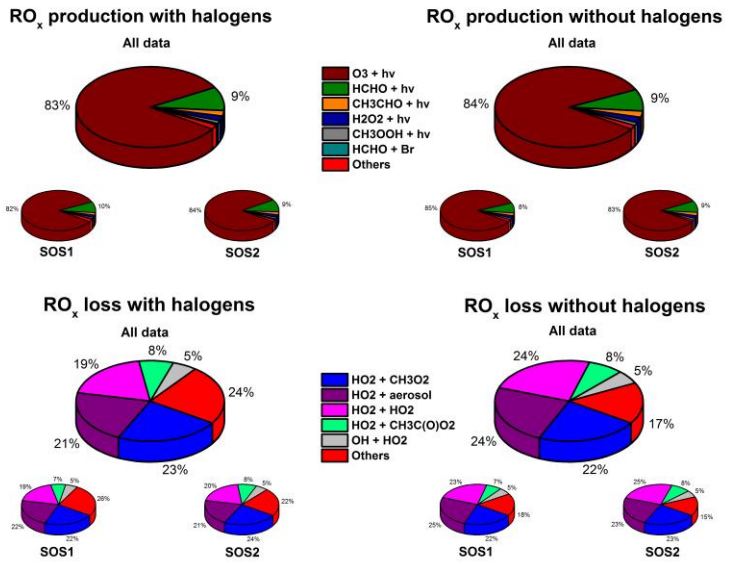

Figure 4: Processes controlling the a) instantaneous RO_x radical production (with RO_x defined here as $OH+HO_2+HOBr+HOI+RO+RO_2$ owing to the rapid processing between HO_2 and HOBr/HOI) around noon (1100-1300 hours) for box model simulations with halogen chemistry; b) the instantaneous RO_x radical production around noon for box model simulations without halogen chemistry; c) the instantaneous RO_x radical loss around noon for box model simulations with halogen chemistry; d) the instantaneous RO_x radical loss around noon for box model simulations without halogen chemistry. The main charts show the average results for SOS1+SOS2, with results for SOS1 and SOS2 shown separately in the inset charts.

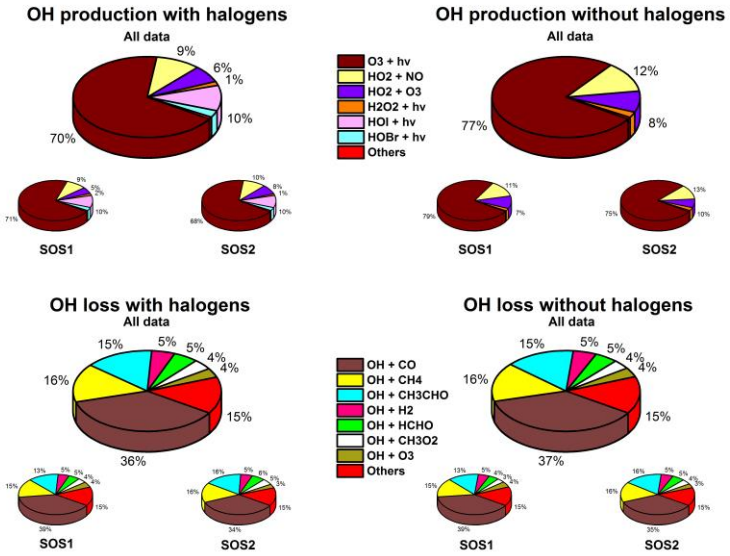

Figure 5: Processes controlling the a) instantaneous OH radical production around noon (1100-1300 hours) for box model simulations with halogen chemistry; b) the instantaneous OH radical production around noon for box model simulations without halogen chemistry; c) the instantaneous OH radical loss around noon for box model simulations with halogen chemistry; d) the instantaneous OH radical loss around noon for box model simulations without halogen chemistry. The main charts show the average results for SOS1+SOS2, with results for SOS1 and SOS2 shown separately in the inset charts.

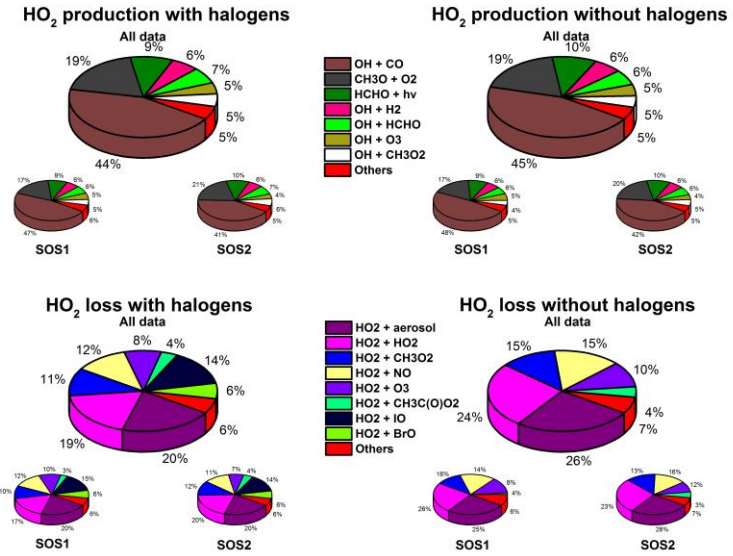

Figure 6: Processes controlling the a) instantaneous HO_2 radical production around noon (1100-1300 hours) for box model simulations with halogen chemistry; b) the instantaneous HO_2 radical production around noon for box model simulations without halogen chemistry; c) the instantaneous HO_2 radical loss around noon for box model simulations with halogen chemistry; d) the instantaneous HO_2 radical loss around noon for box model simulations without halogen chemistry. The main charts show the average results for SOS1+SOS2, with results for SOS1 and SOS2 shown separately in the inset charts.

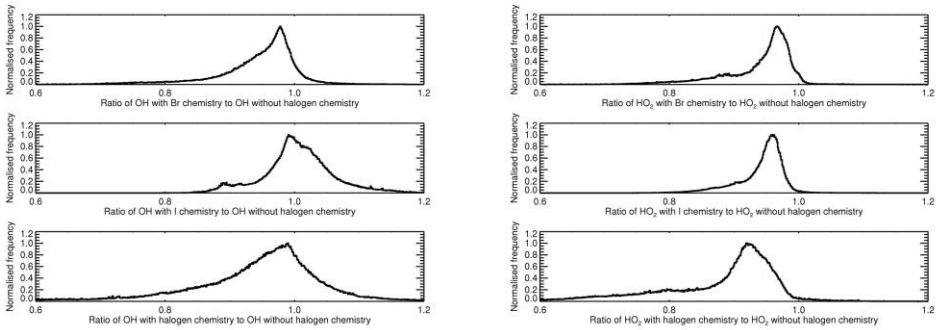

Figure 7: Normalised probability distribution functions showing the fractional changes in OH (left hand side) and HO_2 (right hand side) in GEOS-Chem for all grid boxes on inclusion of bromine chemistry (upper panels), iodine chemistry (middle panels) and bromine and iodine chemistry combined (lower panels).

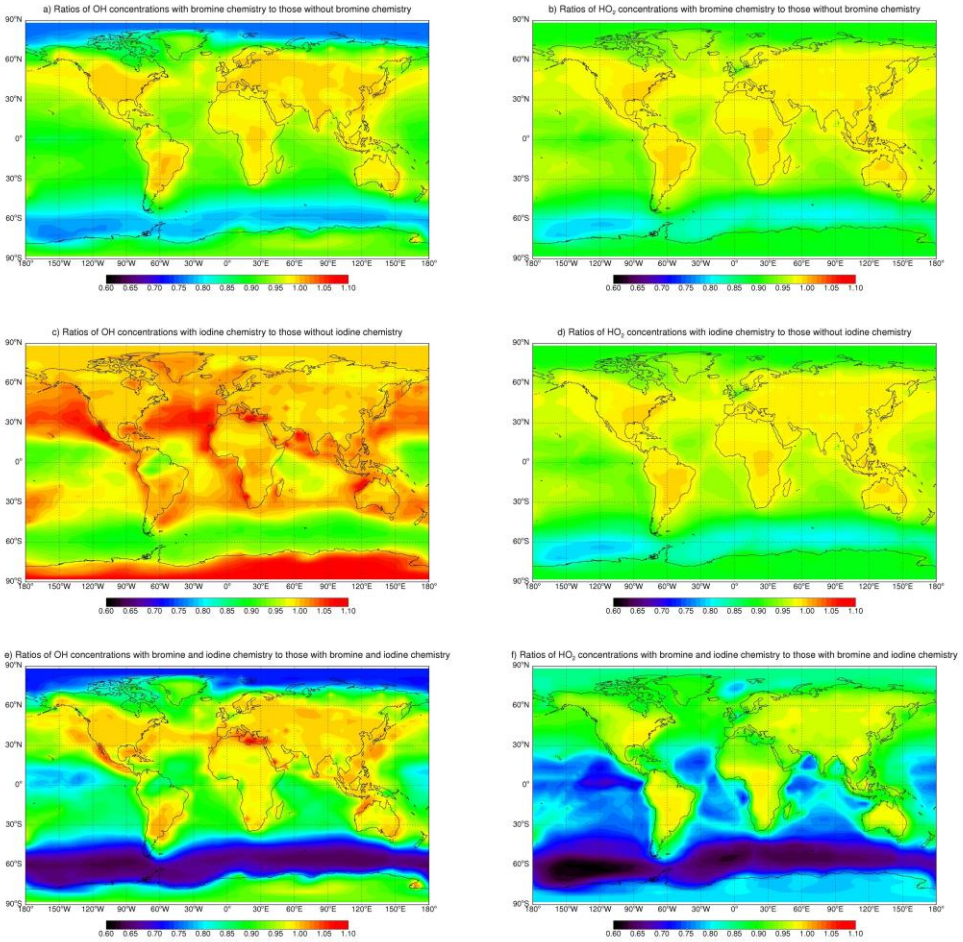

Figure 8: Percentage changes to annual surface layer concentrations of OH (left hand side) and HO_2 (right hand side) in GEOS-Chem on inclusion of bromine chemistry (upper panels), iodine chemistry (middle panels) and bromine and iodine chemistry combined (lower panels).

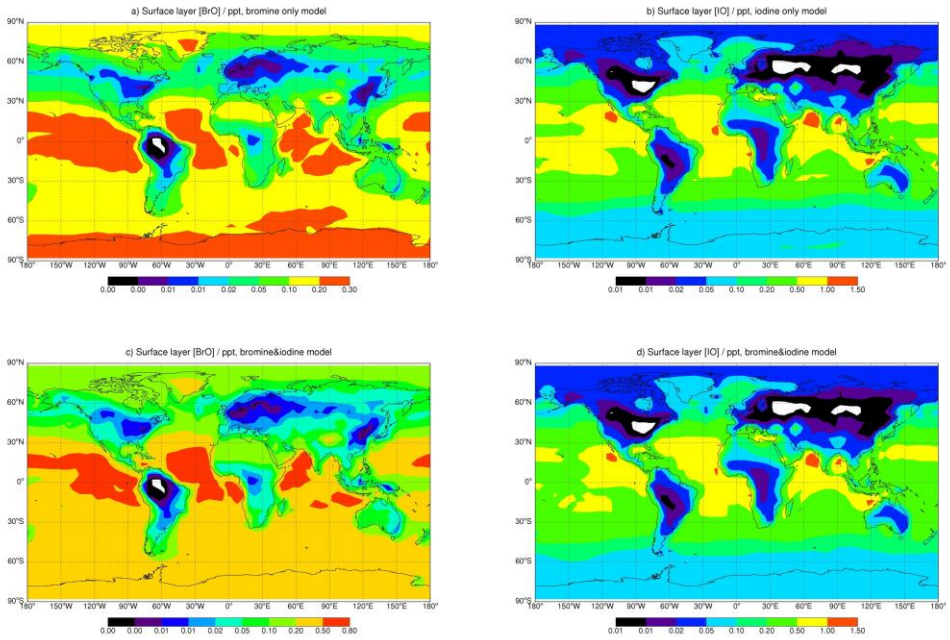

Figure 9: Annual surface layer mixing ratios (ppt) of BrO and IO radicals in GEOS-Chem for model runs with just bromine chemistry (upper left panel), just iodine chemistry (upper right panel) and bromine and iodine chemistry combined (lower panels).

Impacts of bromine and iodine chemistry on tropospheric OH and HO_2: Comparing observations with box and global model perspectives

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Supplementary Material

Speciation of modelled peroxy radicals

Figure S1 shows the speciation of peroxy radicals during SOS determined by the box model. The dominant species at Cape Verde are HO_2 and CH_3O_2, which comprise 87.4 % of the total peroxy radical concentration, and are followed by $CH_3C(O)O_2$ (6.5 %) and $C_2H_5O_2$ (1.1 %), all of which display no HO_2 interference in the laboratory (Whalley et al., 2013; Stone et al., 2014). Any peroxy species potentially contributing to interferences in HO_2 measurements thus constitutes < 4 % of the total peroxy radical concentration, with each species representing < 1 % of the total. Potential interferences arising from conversion of alkene- and aromatic-derived peroxy radicals to OH within the LIF detection cell, as described by Fuchs et al. (2011), are thus expected to be small for SOS and are not explicitly described in the model for this work.

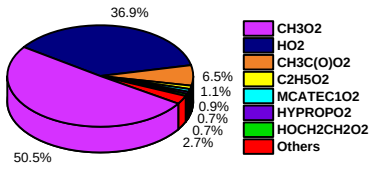

Figure S1: Speciation of peroxy radicals during SOS1 and SOS2. Radical names are as given by the MCM.

Impact of CH_3O_2 + OH

Recent experiments have indicated a rapid reaction between CH_3O_2 and OH (Bossolasco et al., 2014; Fittschen et al., 2014; Assaf et al., 2016; Yan et al., 2016), with the dominant products expected to be CH_3O + HO_2 at an observed yield of (0.8 ± 0.2) (Assaf et al., 2017). As shown in Figures 5 and 6 (main text), this reaction contributes 4 %, on average, to the total midday OH loss during SOS and 5 % to the total HO_2 production, assuming 100 % yield of CH_3O + HO_2. Inclusion of the reaction in the chemistry scheme, for model runs in which halogens are included, decreases the modelled concentration of OH at midday from 5.3 $\times 10^6$ cm^{-3} to 5.2 $\times 10^6$ cm^{-3}, and increases the HO_2 concentration from 3.2 $\times 10^8$ cm^{-3} to 3.9 $\times 10^8$ cm^{-3}.

Figure S2 shows the mean modelled diurnal profile for CH_3O_2 during SOS, for model runs with and without the reaction between CH_3O_2 and OH. Inclusion of the reaction decreases the mean midday CH_3O_2 concentration by 24 %, from 5.7 $\times 10^8$ cm^{-3} to 4.6 $\times 10^8$ cm^{-3}, and thus has a more significant impact on CH_3O_2 than on OH or HO_2. Similar changes to modelled OH, HO_2 and CH_3O_2 were reported by Assaf et al. (2017) using an updated MCM based model for the RHaMBLe campaign in Cape Verde in 2007 (Whalley et al., 2010).

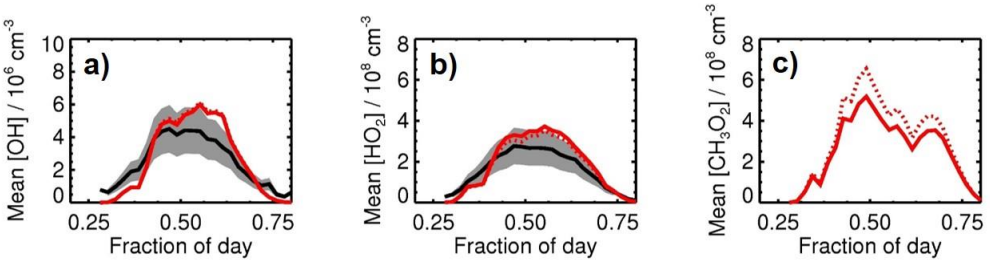

Figure S2: Mean box modelled diurnal profiles for a) OH; b) HO_2; c) CH_3O_2 during SOS (SOS1 and SOS2 combined) for model runs with (red solid line) and without (red broken line) the reaction between CH_3O_2 and OH. For OH and HO_2, observations are shown in black, with grey shading indicating the variability in the observations.

Figure S3 shows the mean midday (1100 to 1300 hours) budgets for CH_3O_2 during SOS for model runs with and without the reaction between CH_3O_2 and OH. Midday production of CH_3O_2, both with and without the reaction between CH_3O_2 and OH, is dominated by CH_3 radical production from CH_4 + OH (~ 55 %), and is followed by the reactions of $CH_3C(O)O_2$ radicals with NO (~ 17 %) and other RO_2 radicals (~ 15 %). Midday loss of CH_3O_2, when CH_3O_2 is included, is dominated by reactions with NO (~ 41 %), HO_2 (~ 33 %), the reaction with OH (~ 15 %), and CH_3O_2 self-reaction (~ 8 %). If the reaction of CH_3O_2 with OH is not included in the model, the loss

reaction with NO represents ~ 48 % of the total CH_3O_2 loss and the reactions with HO_2 and other CH_3O_2 radicals represent ~ 36 % and ~ 12 %, respectively.

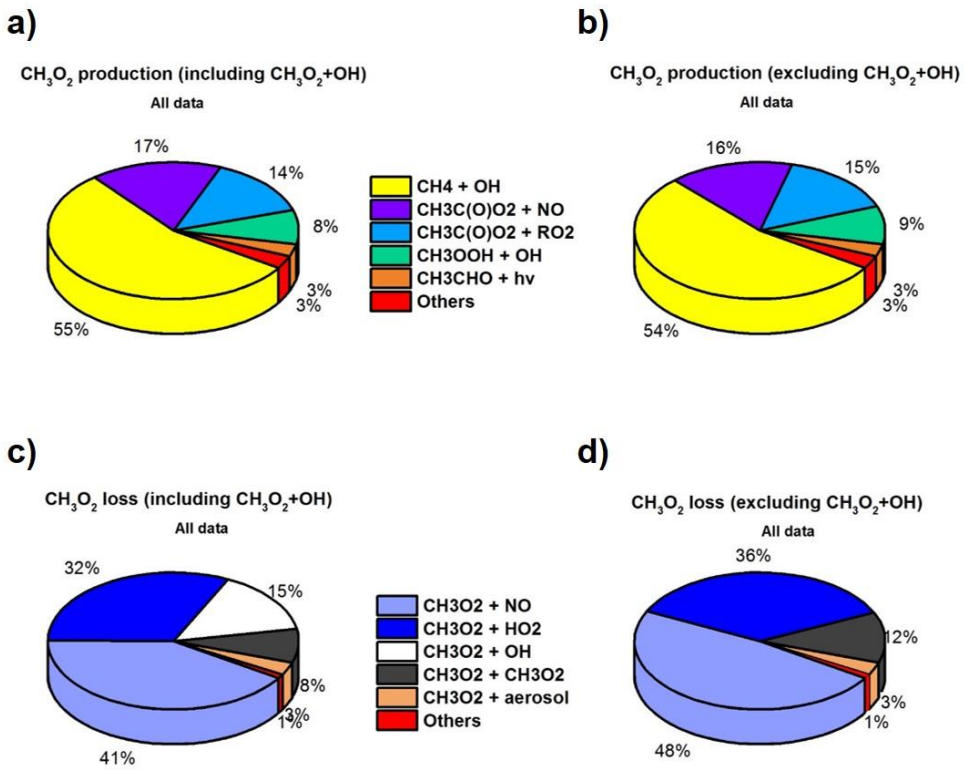

Figure S3: Mean midday (1100 to 1300 hours) budgets for CH_3O_2 during SOS (SOS1 and SOS2 combined). Panel a) production of CH_3O_2 for model runs with the reaction between CH_3O_2 and OH; b) production of CH_3O_2 for model runs without the reaction between CH_3O_2 and OH; c) loss of CH_3O_2 for model runs with the reaction between CH_3O_2 and OH; d) loss of CH_3O_2 for model runs without the reaction between CH_3O_2 and OH.

Time series for observed and box modelled OH and HO_2 radical concentrations

Figures S4 and S5 shows the times series for OH and HO_2 observations and model simulations day-by-day during SOS1 and SOS2.

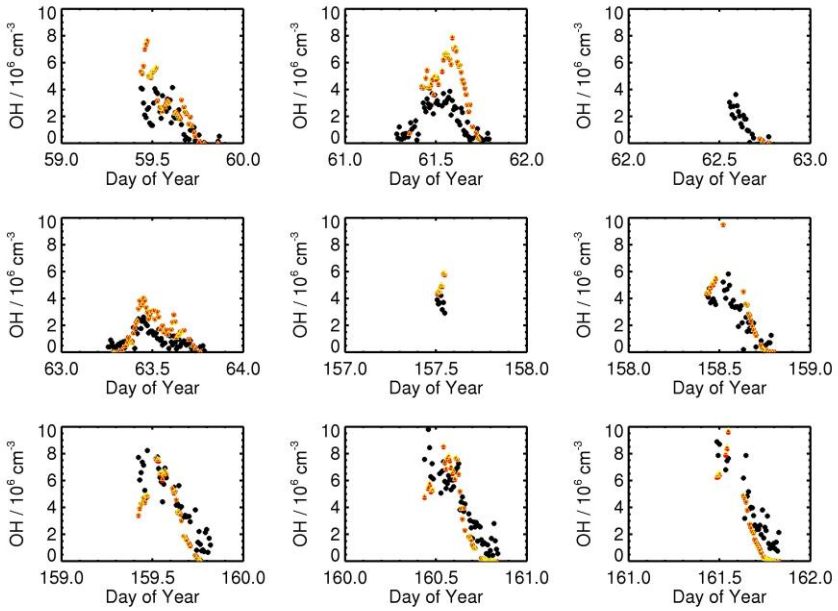

Figure S4: Times series for observed and modelled OH during SOS1 (days 59 to 63) and SOS2 (days 157 to 162). Observed data are shown in black; box model concentrations with halogen chemistry are shown by filled red circles; box model concentrations without halogen chemistry are shown by open yellow triangles.

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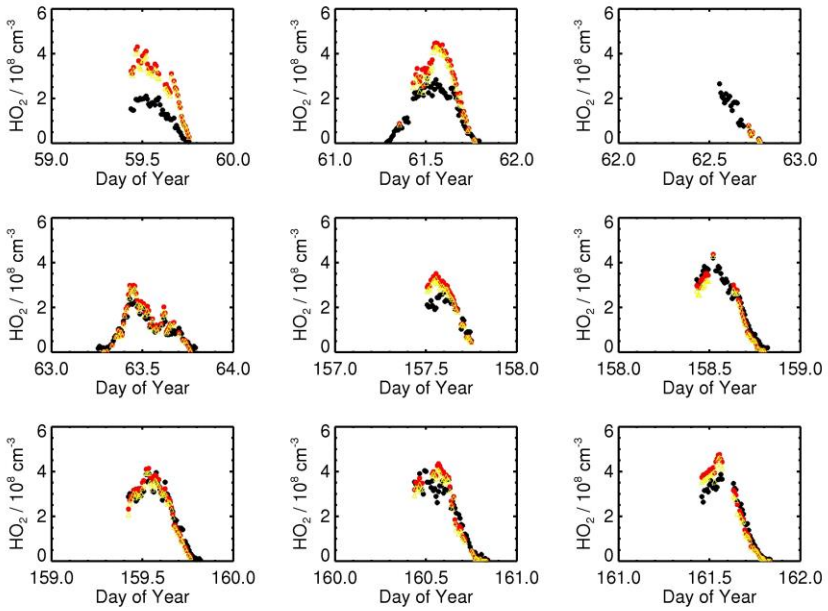

Figure S5: Times series for observed and modelled HO_2 during SOS1 (days 59 to 63) and SOS2 (days 157 to 162). Observed data are shown in black; box model concentrations with halogen chemistry are shown by filled red circles; box model concentrations without halogen chemistry are shown by open yellow triangles.

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Box model sensitivity of OH and HO_2 to BrO and IO mixing ratios

Observations of BrO and IO at the Cape Verde Atmospheric Observatory show average diurnal mixing ratios of 2.5 ppt and 1.4 ppt, respectively, which were used as constraints in the box model simulations presented in this work. In order to test the sensitivity of OH and HO_2 to these constraints, we have performed simulations in which the BrO and IO mixing ratios were constrained to the upper and lower limits of the observed values (3.5 ppt and 1.5 ppt for BrO and 2.0 ppt and 1.0 ppt for IO, as reported by Read et al. (2008) and Mahajan et al. (2010)). In addition, simulations were performed in which mixing ratios of BrO and IO increase from 0600 hours and reach the constant values of 2.5 ppt and 1.4 ppt, respectively, as shown by Read et al. (2008). Results from these simulations are shown in Figure S6, and indicate that there are only minor differences in the OH and HO_2 concentrations between simulations performed on constraining to the upper and lower limits of the observed BrO

and IO concentrations, and that there is little sensitivity of OH or HO_2 to the early morning mixing ratios of BrO and IO.

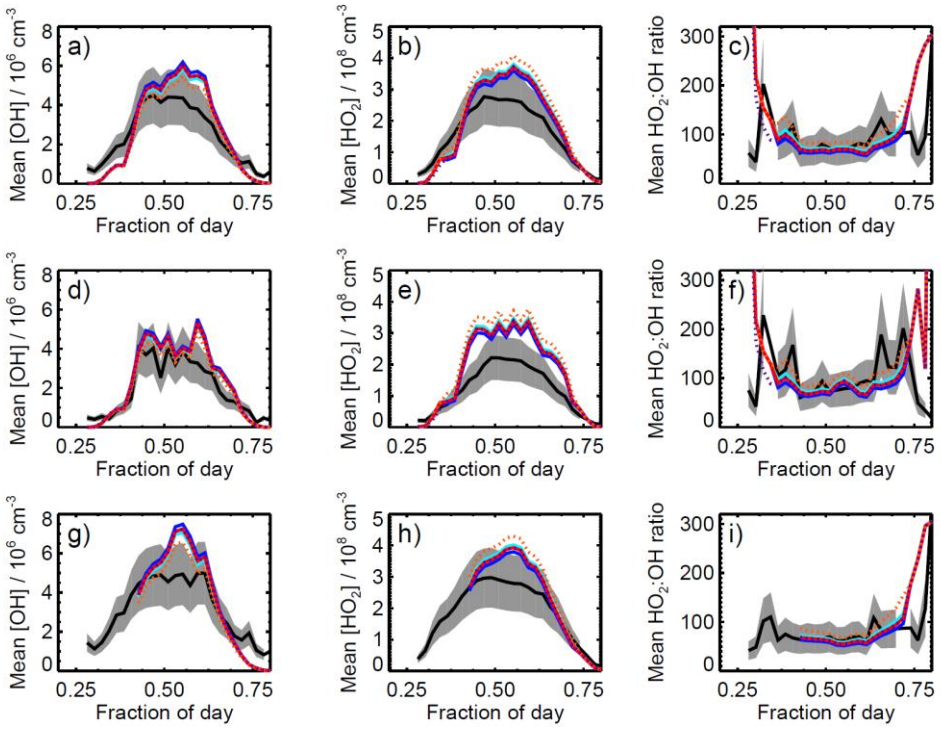

Figure S6: Impacts of changes to BrO and IO constraints on average diurnal profiles for a) OH during both measurement periods; b) HO_2 during both measurement periods; c) HO_2:OH ratio during both measurement periods; d) OH during SOS1 (Feb-Mar 2009); e) HO_2 during SOS1; f) HO_2:OH during SOS1; g) OH during SOS2 (May-June); h) HO_2 during SOS2; i) HO_2:OH ratio during SOS2. Observed data are shown in black, with grey shading indicating the variability in the observations; model simulations constrained to the average daytime (0930 to 1830 hours) mixing ratios of BrO (2.5 ppt) and IO (1.4 ppt) are shown in red; simulations constrained to the upper limits to the daytime mixing ratios of BrO (3.5 ppt) and IO (2.0 ppt) are shown in dark blue; simulations constrained to the lower limits to the daytime mixing ratios of BrO (1.5 ppt) and IO (1.0 ppt) are shown in light blue; simulations constrained to the average daytime mixing ratios of BrO (2.5 ppt) and IO (1.4 ppt) and including increases in the mixing ratios from 0600 hours are shown by the dashed purple lines; simulations with no halogens are shown by the dashed orange lines.

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