

Measurement and modelling of tropospheric reactive halogen species over the tropical Atlantic Ocean

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Abstract. Although tropospheric reactive halogen chemistry is well studied in coastal and polar environments, the presence of halogens over the open ocean environment has not been widely reported. The impacts of halogens on the tropical open ocean marine boundary layer (MBL), in particular, are not well characterised. This paper describes observations of iodine monoxide (IO) and bromine oxide (BrO) over eight months in the tropical open ocean MBL, on the north-eastern side of São Vicente (Cape Verde Islands, 16.85° N, 24.87° W). The highest BrO mixing ratio observed was 5.6 ± 1 pmol mol⁻¹, while the maximum observed IO mixing ratio was 3.1 ± 0.4 pmol mol⁻¹. The average values seen between 09:00–17:00 GMT were ~ 2.8 pmol mol⁻¹ for BrO and ~ 1.5 pmol mol⁻¹ for IO; these averages showed little variability over the entire campaign from November 2006 to June 2007. A 1-dimensional chemistry and transport model is used to study the evolution of iodine species and quantify the combined impact of iodine and bromine chemistry on the oxidising capacity of the MBL. It appears that the measured fluxes of iodocarbons are insufficient to account for the observed levels of IO, and that an additional I atom source is required, possibly caused by the deposition of O₃ onto the ocean surface in the presence of solar radiation. Modelling results also show that the O₃ depletion observed at Cape Verde cannot be explained in the absence of halogen chemistry, which contributes $\sim 45\%$ of the observed

O₃ depletion at the height of measurements (10 m) during summer. The model also predicts that halogens decrease the hydroperoxy radical (HO₂) concentration by $\sim 14\%$ and increase the hydroxyl radical (OH) concentration by $\sim 13\%$ near the ocean surface. The oxidation of dimethyl sulphide (DMS) by BrO takes place at a comparable rate to oxidation by OH in this environment. Finally, the potential of iodine chemistry to form new particles is explored and conditions under which particle formation could be important in the remote MBL are discussed.

1 Introduction

Catalytic cycles involving halogen radicals have been shown to deplete ozone in different regions of the atmosphere. In the 1970s, chlorine chemistry was shown to be the cause of stratospheric ozone depletion (e.g., Molina and Rowland, 1974; Stolarsky and Cicerone, 1974), while over the last three decades bromine chemistry has been shown to cause O₃ depletion events (ODEs) in the polar tropospheric boundary layer (BL) in the Arctic and Antarctic (e.g., Bottenheim et al., 1986; Barrie et al., 1988; Kreher et al., 1997; Tuckermann et al., 1997; Wessel et al., 1998; Frieß et al., 2004; Jones et al., 2006; Saiz-Lopez et al., 2007a). Iodine also occurs at substantial O₃-depleting levels in coastal Antarctica BL (Saiz-Lopez et al., 2007a) and satellite studies show that it can be widespread across the Antarctic continent (Saiz-Lopez et al., 2007b, Schönhardt et al., 2008). Only recently have reactive iodine species been observed at very low levels



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in the Arctic BL (Mahajan et al., 2009a), although it has been observed earlier in the Arctic troposphere (Wittrock et al., 2000). Halogens can also affect the HO_x ratio (i.e., $[\text{HO}_2]/[\text{OH}]$) and NO_x ratio (i.e., $[\text{NO}_2]/[\text{NO}]$). XO (where X=Br, I) radicals oxidise NO to NO_2 , thus increasing the NO_x ratio, while they react with HO_2 to yield HOX, which on photolysis produces OH (e.g. for HOI, the lifetime against photolysis at midday in the tropics is ~ 1.5 min), thus decreasing the HO_x ratio (e.g., Bloss et al., 2005; von Glasow and Crutzen, 2007). In the mid-latitude MBL, BrO has been shown to oxidise DMS up to an order of magnitude faster than OH (Saiz-Lopez et al., 2004; von Glasow et al., 2004). Bromine and iodine chemistry also play a central role in the oxidation of elemental mercury (Hg^0) in the polar atmosphere (Schroeder et al., 1998; Brooks et al., 2006; Saiz-Lopez et al., 2008). Finally, in the coastal MBL, iodine oxides are also implicated in the formation of ultra-fine aerosol, although the exact mechanism is still not understood (e.g., O'Dowd et al., 1998; Hoffmann et al., 2001; Mäkelä et al., 2002; Jimenez et al., 2003; Burkholder et al., 2004; McFiggans et al., 2004; Saunders and Plane, 2005; Sommariva et al., 2006).

The main sources of reactive halogen species can be biogenic emissions of photolabile halocarbons (e.g., Theiler et al., 1978; Wever et al., 1991; Carpenter et al., 1999; Gebhardt et al., 2008) and molecular I_2 (Saiz-Lopez and Plane, 2004), emissions from sea-salt, sea-ice and the ocean surface through acid catalysed reactions or uptake of halogen nitrates (e.g. Behnke et al., 1994; Vogt et al., 1996; Sander and Crutzen, 1996; Abbatt and Nowak, 1997; Fickert et al., 1999; Wennberg, 1999), volcanic emissions (Bobrowski et al., 2003; Lee et al., 2005) and finally anthropogenic emissions (e.g., Andreae et al., 1996; Gabriel et al., 2002). Laboratory experiments have also shown that ozone deposition could play an important role in the emission of halogen compounds, especially iodine from seawater (Garland and Curtis, 1981; Mochida et al., 2000; Martino et al., 2009; Sakamoto et al., 2009).

Relatively high BrO mixing ratios ($> 10 \text{ pmol mol}^{-1}$) are consistently reported in the springtime polar BL (e.g., Hausmann and Platt, 1994; Tuckermann et al., 1997; Richter et al., 1998; Saiz-Lopez et al., 2007a; Wagner and Platt, 1998). BrO has also been measured on a regional scale above salt lakes and in volcanic plumes (Hebestreit et al., 1999; Stutz et al., 2002; Bobrowski et al., 2003). In the mid-latitude MBL, BrO has been positively detected only at three coastal locations: Leser et al. (2003) observed variable levels around the Canary Islands peaking at $2.4 \text{ pmol mol}^{-1}$, Saiz-Lopez et al. (2004) saw post sunrise peak levels of $\sim 6 \text{ pmol mol}^{-1}$ with an average of 2 pmol mol^{-1} over the day at Mace Head, Ireland, while Mahajan et al. (2009b) reported elevated BrO mixing ratios peaking at $7.5 \text{ pmol mol}^{-1}$ in the semi-polluted coastal environment at Roscoff, France. Modelling studies have predicted background BrO levels of $1\text{--}4 \text{ pmol mol}^{-1}$ (Vogt et al., 1996; von Glasow et al., 2002a). Upper lim-

its have also been reported where BrO was not seen above the instrumental detection limit. Theys et al. (2007) reported BrO in the free troposphere (FT) around the Reunion Island with an upper limit of $0.5 \text{ pmol mol}^{-1}$ in the BL. Hönninger (2002) also calculated that BrO around Crete was less than $1.5 \text{ pmol mol}^{-1}$, while Peters et al. (2005) reported an upper limit of 2 pmol mol^{-1} from Lilia, on the coast of Brittany, France.

In the MBL, IO was first detected at Mace Head, Ireland by Alicke et al. (1999). Since then, measurements at a variety of sub-tropical and temperate coastal locations have reported IO levels up to $\sim 27 \text{ pmol mol}^{-1}$ (e.g., Allan et al., 2000; Frieß et al., 2001; Saiz-Lopez and Plane, 2004; Zingler and Platt, 2005; Peters et al., 2005; Stutz et al., 2007; Whalley et al., 2007; Mahajan et al., 2009c). Upper limits for IO have been reported at other locations: $0.8 \text{ pmol mol}^{-1}$ at Crete (Hönninger, 2002), 2 pmol mol^{-1} at Ny-Ålvsund (Wittrock et al., 2000), and 2 pmol mol^{-1} at Kuujuarapik, Canada (Hönninger et al., 2004). In contrast, IO has been observed in excess of 20 pmol mol^{-1} in coastal Antarctica during springtime (Saiz-Lopez et al., 2007a), and satellite measurements have shown that IO can be detected over large areas in and around the continent (Saiz-Lopez et al., 2007b; Schönhardt et al., 2008). Observations of other iodine compounds such as I_2 and OIO are not as common as BrO or IO. OIO was first detected at Cape Grim (Tasmania) by Allan et al. (2001), while the first measurement of I_2 was made by Saiz-Lopez and Plane (2004) at Mace Head. OIO has since been measured in other coastal locations (e.g. Peters et al., 2005; Stutz et al., 2007; Mahajan et al., 2009c), while positive detection of I_2 has been made at only two other locations, Malibu, California (Finley and Saltzman, 2008) and Roscoff, Brittany (Mahajan et al., 2009c).

A recent study at the Cape Verde Islands reported the presence of both BrO and IO at mixing ratios of $1\text{--}3 \text{ pmol mol}^{-1}$, and indicated that the observed ozone depletion during the same campaign could not be explained in the absence of halogen compounds (Read et al., 2008). The importance of this study is that this was arguably the first measurement of these halogen radicals in the mid-ocean MBL where local biological sources (such as macroalgae exposed at low tide) were unimportant, and hence may be representative of halogen activity over much of the open ocean (Read et al., 2008). In the present paper, we consider these halogen oxide measurements at Cape Verde in further detail, using a 1-D model to investigate the source strengths and likely vertical distributions of iodine species in the tropical Atlantic MBL. We then explore the effects of combined iodine and bromine chemistry on O_3 depletion, the HO_x ratio and the lifetime of DMS. Finally, we consider the potential for iodine oxides to form new particles which may grow to become cloud condensation nuclei (CCN) in this environment.

2 Experimental

DOAS measurements of BrO and IO were made at Cape Verde for a period of eight months from November 2006 to June 2007, as part of the UK Surface Ocean Lower Atmosphere Study (SOLAS) programme. During this period, the instruments were located at the Cape Verde Atmospheric Observatory (CVAO) (16.85° N, 24.87° W), on the north-eastern side of the island of São Vicente. Further details about the observatory and the prevalent meteorological conditions can be found elsewhere (Lee et al., 2010). The long-path DOAS instrument (LP-DOAS) was placed in a temperature-controlled sea freight container at the observatory. The optical path ran across the bay, where a retro-reflector array was placed at a distance of 6 km from the measurement site (Supporting online text Fig. S1 <http://www.atmos-chem-phys.net/10/4611/2010/acp-10-4611-2010-supplement.pdf>), resulting in a total optical path length of 12 km. The light beam was ~ 10 m above the ocean surface. Further details on the LP-DOAS and the deconvolution procedure used can be found elsewhere (Plane and Saiz-Lopez, 2006). Briefly, the recorded spectra were converted into optical densities, and the contributions of the individual absorbing species were then determined by using singular value decomposition to fit simultaneously a library of reference absorption cross-sections. For the retrieval of BrO, the 324–357 nm spectral window was used, while IO was retrieved in the 425–445 nm window. Reference spectra included in the fitting routine for retrieving BrO were: BrO (Wilmouth et al., 1999), NO₂ (Vandaele et al., 1998), O₃ (Daumont et al., 1992), HONO (Bongartz et al., 1991) and HCHO (Cantrell et al., 1990). For retrieving IO, reference spectra were: IO (Gómez Martin et al., 2005), NO₂ (Harder et al., 1997) and H₂O (Rothman et al., 2003). An example of the quality of the fits, along with averaged diurnal and annual measurements are presented elsewhere (Read et al., 2008).

During the summer of 2007 (May), an intensive campaign took place at the observatory as a part of the Reactive Halogens in the Marine Boundary Layer (RHAMBLe) project. The details of the instruments deployed during this period can be found in Lee et al. (2010). Along with other ancillary measurements, the intensive campaign also involved a research aircraft that measured composition over the site to assess how representative of the overlying BL it was and to determine any diurnal variability in BL depth. Additionally, a ship-based study measured the fluxes of halocarbons above the ocean surface around Cape Verde and over the upwelling region near Mauritania during the same period (Jones et al., in preparation).

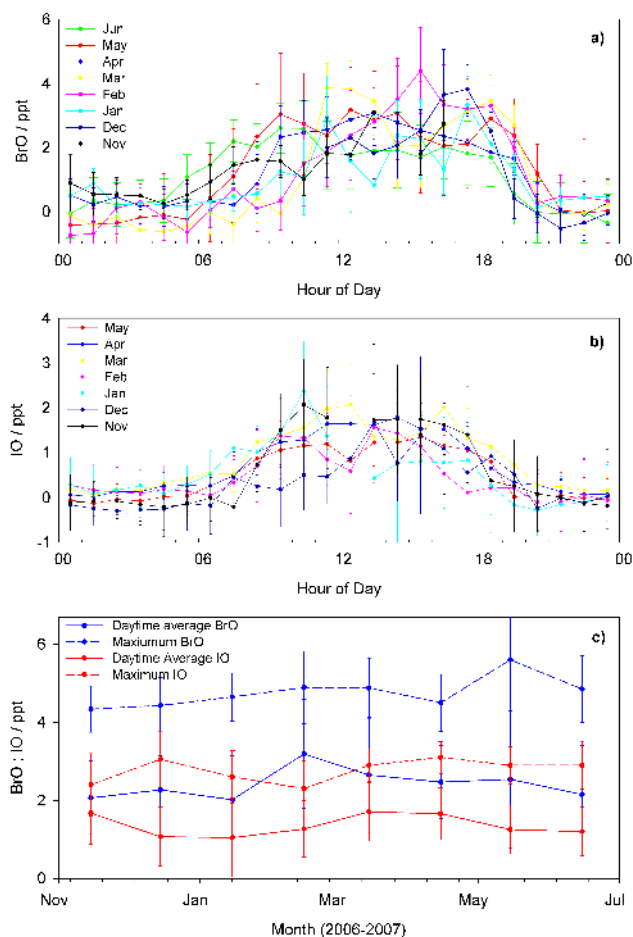


Fig. 1. The monthly averaged diurnal profiles for IO and BrO are shown in panels (a) and (b). Both radicals show a distinctive top-hat profile with the highest mixing ratios measured between 09:00–17:00 GMT. The average annual profile of IO and BrO along with the highest measured mixing ratio for each month is shown in panel (c) indicating little annual variability. Local noon is at GMT-1. The average detection limits were BrO: $0.5\text{--}1.0\text{ pmol mol}^{-1}$ and IO: $0.3\text{--}0.5\text{ pmol mol}^{-1}$.

3 Observations

BrO was detected on a total of 38 days, while IO was detected on 56 days over the duration of the campaign. The maximum BrO mixing ratio observed was $5.6\pm 1\text{ pmol mol}^{-1}$ (27 May 2007), while the maximum IO mixing ratio observed was $3.1\pm 0.4\text{ pmol mol}^{-1}$ (15 April 2007). Figure 1a and b illustrate the measured monthly-averaged diurnal profiles of BrO and IO, respectively, for the eight months of the campaign. BrO and IO were observed above the detection limit whenever the solar zenith angle was less than $\sim 92^{\circ}$, i.e., twilight and full daylight conditions. Although there was considerable day-to-day variation throughout the campaign (higher temporal resolution data in supporting online material, Figs. S2–S9 <http://www.atmos-chem-phys.net/>

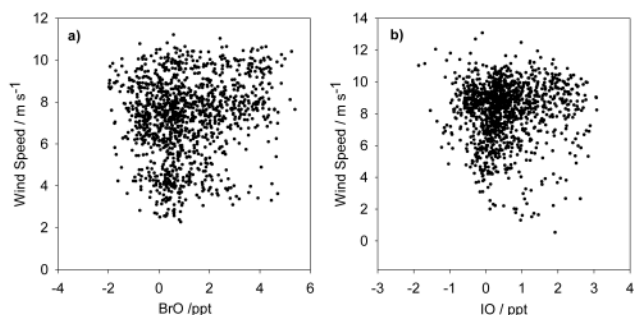


Fig. 2. Correlation of BrO and IO with wind speed at São Vicente. Panel (a) shows the correlation for BrO and (b) show a similar plot for IO. There is no significant correlation for either species: for [BrO] vs. wind speed, linear regression through the data has an $R^2=0.02$, while for [IO] vs. wind speed, $R^2=0.003$.

10/4611/2010/acp-10-4611-2010-supplement.pdf), it can be seen that the profiles exhibit a “top-hat” distribution, with the mixing ratios roughly representing a plateau showing little change between 09:00–17:00 GMT. On averaging the data over the entire campaign, both species show similar diurnal profiles dependent on solar radiation, with mixing ratios below the detection limits (BrO: 0.5–0.8 pmol mol⁻¹, IO: 0.3–0.5 pmol mol⁻¹) at night and average peak values of ~2.8 pmol mol⁻¹ BrO and ~1.5 pmol mol⁻¹ IO during the daytime (Read et al., 2008). The monthly daytime-averaged values between 09:00 and 17:00 GMT, and the maximum observed mixing ratios in each month of the campaign, are shown for both species in Fig. 1c. There is clearly very little seasonal variation: although there is some hint of slightly higher values during spring (February–May), this is not significant within the variability of the observations.

The BrO and IO mixing ratios do not show a strong correlation with the origin of the air masses given by the air mass back trajectories, the wind direction or the wind speed. Figure 2 shows the variation of BrO and IO with wind speed. There is no significant correlation for either species: for [BrO] vs. wind speed, linear regression through the data has a slope of 0.21 ± 0.04 and $R^2=0.02$, while for [IO] vs. wind speed the slope was 0.12 ± 0.06 and $R^2=0.003$. In the case of BrO, all measurements were made when the wind happened to be from the prevailing north-easterly direction, and hence a correlation analysis cannot be made. In the case of IO, although the wind direction did vary, there does not appear to be clear dependence on wind direction.

Finally, the LP-DOAS was also periodically configured to measure other iodine species (I₂ and OIO), as well as the night-time radical NO₃. All three species were below the detection limit of the instrument throughout the campaign i.e. [I₂] ≤ 15 pmol mol⁻¹, [OIO] ≤ 10 pmol mol⁻¹, and [NO₃] ≤ 4 pmol mol⁻¹.

4 Discussion and modelling

4.1 Bromine chemistry

The release of inorganic bromine from sea-salt aerosols and its impact on the remote MBL has been studied in some detail in previous work (Sander et al., 2003; Vogt et al., 1996; von Glasow et al., 2002a; von Glasow et al., 2002b; von Glasow et al., 2004). Some model studies for the acid-catalysed activation of bromine from sea-salt aerosol have predicted BrO mixing ratios in the MBL ranging from 1–4 pmol mol⁻¹, with a diurnal top-hat variation (Vogt et al., 1996; von Glasow et al., 2002a; Yang et al., 2005). This is due to the removal of BrO via the reaction with HO₂ to form HOBr, which peaks at midday and limits the build up of BrO. Box model calculations for conditions seen at Cape Verde show that to sustain an average [BrO] of ~2.8 pmol mol⁻¹, there needs to be a total gas-phase bromine loading of ~10 pmol mol⁻¹. Considering that the [Br⁻]/[Cl⁻] ratio in fresh aerosols is ~1.5 × 10⁻³ mol mol⁻¹, reflecting the sea water ratio of 1:660 (Wilson, 1975), and assuming an increased salinity of 320 g l⁻¹ due to evaporation of water from sea-salt aerosols, the maximum amount of bromide available in 20 μm³ cm⁻³ of wet aerosol volume (Allan et al., 2009) would be ~4 pmol mol⁻¹. Hence, continuous replenishment of aerosols and depletion of bromide from these aerosols would explain the levels of BrO seen at Cape Verde considering the long lifetime of bromine in the gas phase (~10 d in the tropics; von Glasow et al., 2004). Br⁻ depletion in aerosols can occur through acid-catalysed reactions, which are pH-dependent (Mozurkewich, 1995; Abbatt and Waschewsky, 1998; Fickert et al., 1999). Br⁻ depletion in aerosols has been reported previously (Gabriel et al., 2002; Newberg et al., 2005). Furthermore, measurements of total gaseous inorganic Br made at Cape Verde during May 2007 indicate that the total inorganic Br present at Cape Verde was as high as 12 pmol mol⁻¹ (A. A. P. Pszeny, University of New Hampshire and W. C. Keene, University of Virginia, personal communication, 2009), indicating that the observed BrO levels can satisfactorily be explained through emissions from sea-salt aerosol. It should be noted that recent measurements in the tropical Atlantic Ocean have reported [BrO] peaking at 10.2 nmol mol⁻¹ near the African coast, suggesting other possible sources (Martin et al., 2009). Since the focus of the modelling study described below is iodine chemistry, we will therefore not explicitly model bromine aerosol chemistry here. Instead, the model will be constrained with the BrO observations, and then used to explore the iodine source required to replicate the IO measurements and to study the combined impact of iodine and bromine chemistry on O₃, HO_x and DMS chemistry. [BrO] is set to peak at 2.8 pmol mol⁻¹ with a daytime profile showing little change in mixing ratios from 09:00–17:00 GMT according to observations at Cape Verde and is considered to be well mixed in the boundary layer due to the long lifetime of inorganic

bromine in the gas phase, which is ~ 10 days in the tropics (von Glasow et al., 2004).

4.2 Iodine chemistry

Measurements and modelling studies of IO over the open ocean are rare, and the impacts of iodine chemistry on the remote oceanic environment have not been studied in detail. Although the levels of IO reported here are in accord with previous measurements along the coasts of Tenerife and Tasmania (Allan et al., 2000), no studies have been performed in the tropical remote MBL and to our knowledge these are the first measurements of reactive iodine species (RIS) over the tropical open ocean. The presence of IO above the detection limit of the instrument ($0.3\text{--}0.5\text{ pmol mol}^{-1}$) at Cape Verde is surprising as the sources of iodine are assumed to be mainly biogenic. Although the oceans around Cape Verde are biologically active (Fallowski, 1997), there are no large macroalgal beds around São Vicente due to its steep shelf. Hence, it is probable that these waters represent a large area of elevated iodine emissions, possibly much of the tropical open oceans. A recent study by Martino et al. (2009) has suggested that deposition of O_3 on the ocean surface could lead to the emission of iodocarbons in the presence of dissolved organic matter, which on photolysis could contribute to RIS in the MBL. Fluxes of iodocarbons measured over the open ocean close to the measurement site, as a part of the RHAMBLE campaign, confirm their presence (Jones et al., 2010) and indicate that they could indeed act as a source of RIS in the remote MBL.

The Tropospheric HALOgen chemistry MOdel (THAMO) is now employed to test whether the levels of IO seen at Cape Verde can be explained by the measured iodocarbon fluxes. Further details about THAMO can be found in Saiz-Lopez et al. (2008). Briefly, it is a 1-D chemistry transport model with 200 stacked boxes at a vertical resolution of 5 m (total height 1 km). The model treats iodine, bromine, O_3 , NO_x and HO_x chemistry using 210 reactions. The chemical scheme used for this study is from Saiz-Lopez et al. (2008) and is updated according to Mahajan et al. (2009c). The model is constrained with typical measured values of other chemical species: $[\text{CO}] = 110\text{ nmol mol}^{-1}$; $[\text{DMS}] = 30\text{ pmol mol}^{-1}$; $[\text{CH}_4] = 1820\text{ nmol mol}^{-1}$; $[\text{ethane}] = 925\text{ pmol mol}^{-1}$; $[\text{CH}_3\text{CHO}] = 970\text{ pmol mol}^{-1}$; $[\text{HCHO}] = 500\text{ pmol mol}^{-1}$ (measured during summer by the LP-DOAS at the CVAO); $[\text{isoprene}] = 10\text{ pmol mol}^{-1}$; $[\text{propane}] = 60\text{ pmol mol}^{-1}$; $[\text{propene}] = 20\text{ pmol mol}^{-1}$ (Read et al., 2008; Lee et al., 2010; Read et al., 2009). Wind speed measurements collected at three heights (4, 10 and 30 m) were used to construct an eddy diffusion coefficient (K_z) profile (Stull, 1988), shown in the supporting online text (Fig. S10 <http://www.atmos-chem-phys.net/10/4611/2010/acp-10-4611-2010-supplement.pdf>). The average background aerosol surface area (ASA) used is $1 \times 10^{-6}\text{ cm}^2\text{ cm}^{-3}$, an average value estimated from Allan

et al. (2009). During the RHAMBLE campaign, aircraft measurements of temperature in the BL revealed a strong temperature inversion about 1 km from the surface (Read et al., 2008), indicating that the BL at Cape Verde is decoupled from the free troposphere. Hence, the K_z profile is assumed to increase up to a height of 30 m (where it peaks at $3 \times 10^4\text{ cm}^2\text{ s}^{-1}$), after which it decreases at a constant rate to a value of $2\text{ cm}^2\text{ s}^{-1}$ at the top of the BL (Fig. S10 <http://www.atmos-chem-phys.net/10/4611/2010/acp-10-4611-2010-supplement.pdf>). The sensitivity of the model to the K_z profile is discussed later. The model is used to replicate the average levels of IO seen during May as there was a suite of other trace gas measurements made during this period (Lee et al., 2010), although it should be noted that there was little variability in the diurnal profiles of IO and BrO throughout the campaign (Fig. 1). The model is initialised at midnight and the evolution of iodine species, O_3 , NO_x and HO_x is followed for a period of 48 h.

Initially, the injection of iodine into the model is constrained using the average sea-air iodocarbon fluxes measured over the open ocean close to Cape Verde (Jones et al., 2010): $\text{CH}_2\text{I}_2 = 13.0\text{ nmol m}^{-2}\text{ d}^{-1}$, $\text{CH}_2\text{IBr} = 10.9\text{ nmol m}^{-2}\text{ d}^{-1}$, $\text{CH}_2\text{ICl} = 16.2\text{ nmol m}^{-2}\text{ d}^{-1}$, $\text{CH}_3\text{I} = 48.5\text{ nmol m}^{-2}\text{ d}^{-1}$, $\text{C}_2\text{H}_5\text{I} = 4.1\text{ nmol m}^{-2}\text{ d}^{-1}$ and $1\text{-C}_3\text{H}_7\text{I} = 0.9\text{ nmol m}^{-2}\text{ d}^{-1}$. The predicted vertical profiles of the iodocarbons are shown in the supporting online text (Fig. S11 <http://www.atmos-chem-phys.net/10/4611/2010/acp-10-4611-2010-supplement.pdf>). The longer lived iodocarbons (e.g. $\text{C}_2\text{H}_5\text{I}$) are better mixed through the BL, but the more photo-labile iodocarbons show a strong diurnal profile and are limited to $< 300\text{ m}$ (CH_2I_2 , CH_2IBr , CH_2ICl). Using these measured iodocarbon fluxes, the predicted levels of daytime IO are only $\sim 30\%$ of the observed values, peaking at only $0.45\text{ pmol mol}^{-1}$ compared to the average observed value of around 1.5 pmol mol^{-1} (Fig. 3). The predicted daytime O_3 depletion is only $\sim 2.9\text{ nmol mol}^{-1}$, compared to an observed decrease of $\sim 4.5\text{ nmol mol}^{-1}$ observed at Cape Verde during May 2007 (Read et al., 2008). Additionally, the diurnal profile indicates that the IO should peak later in the evening (Fig. 3) due to a slow release of I atoms resulting from the relatively long lifetime of the iodocarbons (e.g. $\text{CH}_2\text{IBr} \sim 15\text{ min}$, $\text{CH}_2\text{ICl} \sim 1\text{ h}$, $\text{CH}_3\text{I} = 23\text{ h}$ at midday) and hence slow build-up of IO during the daytime, in contrast to the observed top-hat profile (Figs. 1 and 3).

These modelling results show that an additional flux of iodine is necessary in order to reproduce the observed levels of IO, as the iodocarbons can account for around one third of the observed IO mixing ratio. In the model, this additional source is considered to be in the form of an I_2 flux from the sea. Several laboratory studies have shown that deposition of O_3 on sea surface leads to the emission of I_2 (Garland and Curtis, 1981; Sakamoto et al., 2009). If a constant day and night I_2 flux of $5 \times 10^7\text{ molecules cm}^{-2}\text{ s}^{-1}$ is considered, the model predicts a peak of 1.6 pmol mol^{-1} of IO during the

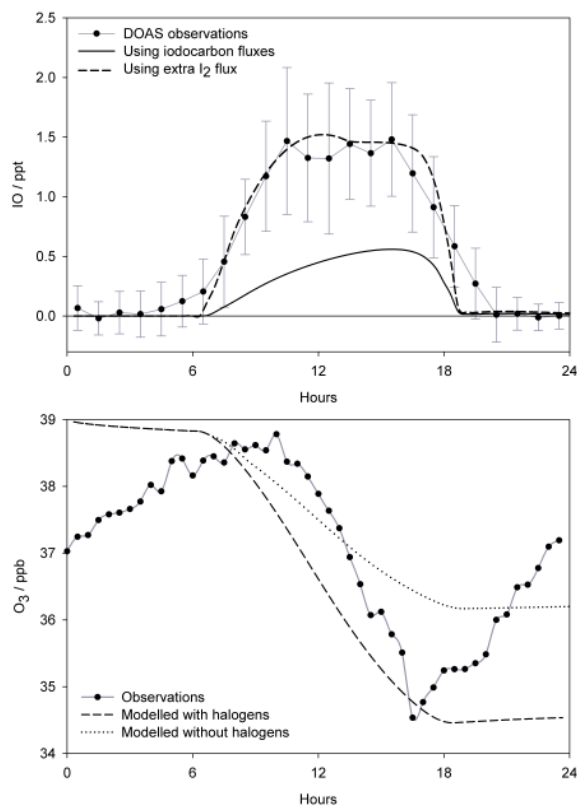


Fig. 3. Observed diurnal IO mixing ratios and O₃ destruction during May 2007 at Cape Verde (Read et al., 2008) compared with model predicted O₃ at the height of measurements (10 m). In the absence of halogens, the model predicts the loss of only 2.5 nmol mol⁻¹ in one day, while in the presence of halogens, this loss is ~4.4 nmol mol⁻¹. Local noon is at GMT-1.

day time, which is in agreement with the observations. In this scenario, the model also predicts a post-sunrise pulse of ~1.4 pmol mol⁻¹ lasting for about 20 min. The best fit to the observed data is achieved by using a flux considered to be active only during the daytime. There is evidence for the photosensitized production of volatile halogen species at the sea surface (Reeser et al., 2009). If this source dominated (or worked in conjunction with) O₃ deposition, it would account for a significant diurnal source of iodine. An I₂ flux peaking at 5.7×10^8 molecule cm⁻² s⁻¹ is needed along with the measured iodocarbon flux to reproduce the observed IO. The diurnal profile of this flux is chosen to produce the IO observations and peaks between 09:00–00:00 GMT with zero emissions during the night time (supplementary online text Fig. S12 <http://www.atmos-chem-phys.net/10/4611/2010/acp-10-4611-2010-supplement.pdf>). Figure 4 shows the predicted diurnal vertical profiles for IO, O₃, I₂ and OIO when this additional flux is included. Now, the levels of IO are in good accord with the observations at the height of measurements. The predicted vertical profile of IO shows a strong gradient with only 0.15 pmol mol⁻¹

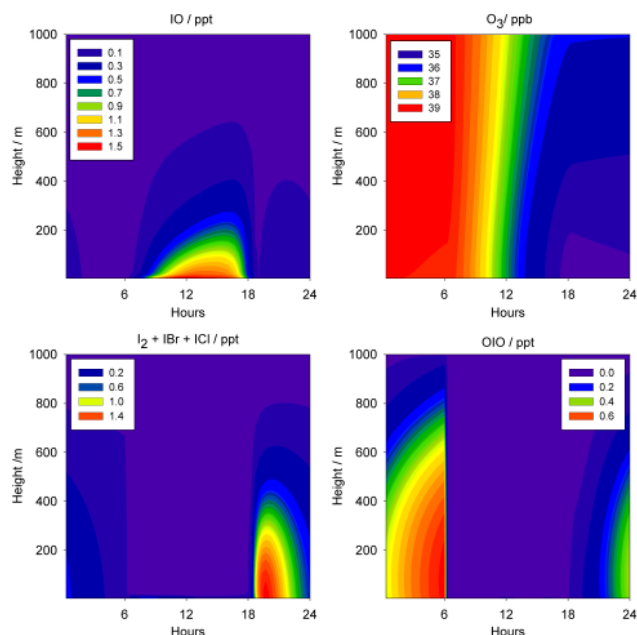


Fig. 4. Predicted profiles of IO, O₃, (I₂+IBr+ICl) and OIO at Cape Verde using an extra I₂ flux in addition to measured halocarbon fluxes. The IO mixing ratios are seen to peak at 1.5 pmol mol⁻¹ at the height of measurements and are in good accord with the observed average of ~1.5 pmol mol⁻¹. The predicted O₃ depletion is about 4.4 nmol mol⁻¹ over one day, while the predicted I₂ and OIO values are under the detection limit of the DOAS instrument (I₂–15 pmol mol⁻¹, OIO–10 pmol mol⁻¹). The model is initialised at midnight and the IO, OIO and (I₂+IBr+ICl) data from 24–30 h has been shifted by –24 h in order to illustrate the full diurnal cycle. Local noon is at GMT-1.

(10%) seen at 500 m (Figs. 4 and 5). Even with the additional I₂ flux, the I₂ and OIO levels are under the detection limit throughout the BL. It should also be noted that even when using a continuous I₂ flux, the I₂ mixing ratio predicted by the model during the night at 10 m is still under the DOAS detection limit. The K_z profile in Fig. S10 (<http://www.atmos-chem-phys.net/10/4611/2010/acp-10-4611-2010-supplement.pdf>) considers that the K_z reduces with height after 30 m but the model was found to be sensitive to the height from which the K_z is considered to decrease. For an extreme condition, we assume that the K_z does not decrease with height, but stays constant after 30 m. Using such a profile, the predicted [IO] at the height of measurements (10 m) is found to be ~18% lower at the peak of the I atom flux due to faster mixing. However, no realistic diurnally-changing K_z profile can reproduce the observed IO profile using only the iodocarbon fluxes.

Considering an O₃ deposition velocity of 0.05 cm s⁻¹ (Chang et al., 2004) and an O₃ mixing ratio of 35 nmol mol⁻¹ in the BL, the total flux of O₃ molecules into the ocean would be 4.3×10^{10} molecules cm⁻² s⁻¹. If the deposition of O₃ is responsible for the emission of I atoms from the

ocean, this would mean that ~ 3 iodine atoms are emitted to the gas phase for every 100 molecules of O_3 that are deposited on the ocean surface. One laboratory study has suggested that 20% of the O_3 deposited to the ocean surface reacts with I^- ions in seawater to form molecular iodine and suggested that a significant fraction of this evaporates from the ocean surface (Garland and Curtis, 1980). Furthermore, the best fit of the I_2 flux to the measured IO diurnal profile requires that the emission of I atoms from the ocean surface is more active during the daytime (Fig. S12 <http://www.atmos-chem-phys.net/10/4611/2010/acp-10-4611-2010-supplement.pdf>), which could indicate a photochemical production of I_2 or other iodocarbons in the sea-surface micro layer, perhaps coupled with the deposition of O_3 .

The vertical profile of iodine species is shown in Fig. 5. It can be seen that the IO mixing ratio drops to about 10% of the value at the surface in the first 500 m, so that most of the IO is confined to the lower BL. The total column abundance predicted by the model is 9.7×10^{11} molecules cm^{-2} , which is below the upper limit of 2×10^{12} molecules cm^{-2} for current satellite measurements (Schönhardt et al., 2007).

4.3 Effect of halogens on ozone

The vertical temperature profiles measured by the aircraft show a capped BL with a strong temperature inversion at about 1000 m during all the flights above Cape Verde indicating that the BL is decoupled from the free troposphere (Read et al., 2008). Read et al. also concluded that the MBL around Cape Verde is subject to minimal diurnal variations in dynamics because the temperature and wind speed are relatively constant. Furthermore, the free tropospheric O_3 mixing ratios over Cape Verde were found to be significantly lower than in the BL (Read et al., 2008), indicating that O_3 entrainment cannot take place into the BL directly above Cape Verde. O_3 entrainment into the BL actually takes place around 200 km further north-east of the measurement site, where measurements show elevated O_3 in the free troposphere (Lee et al., 2010); advection of air to Cape Verde then causes a rise in the O_3 concentrations during the night (Read et al., 2008).

During the summer month of May, the average loss of O_3 is ~ 4.3 nmol mol^{-1} day^{-1} , although in the absence of halogens, the model predicts a loss of only ~ 2.5 nmol mol^{-1} over the entire day at the height of measurements (Fig. 3). This calculated O_3 loss is due to HO_x chemistry and deposition to the ocean surface. If the observed levels of halogens are now included in the model, through emission of iodine as explained earlier (1.5 pmol mol^{-1} IO and constrained 2.5 pmol mol^{-1} BrO), the calculated O_3 depletion at the height of measurements increases to ~ 4.5 nmol mol^{-1} day^{-1} (Fig. 3). The catalytic cycles involving halogens cause an increased loss of 1.6 nmol mol^{-1} day^{-1} and the total predicted O_3 loss is now in good agreement with the ob-

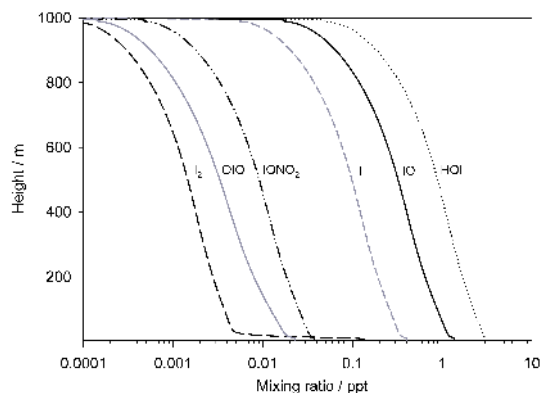


Fig. 5. Modelled vertical profiles of iodine species at Cape Verde are shown. The IO mixing ratios are seen to reduce to 10% at 500 m, while OIO and I_2 would be under the detection limit of the DOAS instrument (I_2 —15 pmol mol^{-1} , OIO—10 pmol mol^{-1}) all through the BL.

served loss. Figure 4 also shows that this observed depletion is well mixed in the BL with a maximum difference of 1.2 nmol mol^{-1} between the surface and at 1 km. This prediction is confirmed by the aircraft measurements, which showed that O_3 is well-mixed in the BL (Read et al., 2008). A point to note is the significant role that iodine chemistry plays in the O_3 depletion. At midday, the O_3 destruction rate due to iodine alone is 0.1 nmol mol^{-1} $hour^{-1}$, while the destruction due to bromine alone is 0.028 nmol mol^{-1} $hour^{-1}$. The combined impact of both halogens due to catalytic cycles involving IO and BrO (Gilles et al., 1997) destroys O_3 at a rate of 0.19 nmol mol^{-1} $hour^{-1}$.

4.4 Effect on HO_x

In situ measurements of OH and HO_2 were performed at Cape Verde during the RHAMBLE campaign using the LIF technique (Whalley et al., 2010). The measurements were made at the height of 10 m above sea level. Typical peak noon values of 0.25 pmol mol^{-1} and 18 pmol mol^{-1} were measured for OH and HO_2 , respectively. BrO and IO react with HO_2 to form HOBr and HOI, which on photolysis reproduce OH, thus reducing the HO_x ratio (HO_2/OH) ratio. Figure 6 shows the effect of halogen chemistry on the vertical profile of OH and HO_2 , for scenarios with and without halogens. At the height of the measurements, the model scenario without halogen chemistry over-predicts HO_2 by $\sim 14\%$ of the measured concentration, and under-predicts the OH by $\sim 13\%$. Thus, the modelled HO_x ratio is 94, compared with the measured ratio of 72 (Whalley et al., 2010). When halogen chemistry is included, the calculated OH and HO_2 levels and diurnal profile are in agreement with the observations: the modelled ratio is now 76. Figure 6 also shows that the vertical profile of OH and HO_2 are significantly different when halogens are included in the model, with the lowest predicted HO_x ratio closer to the surface, although at the top of the BL the effect of halogens is greatly reduced.

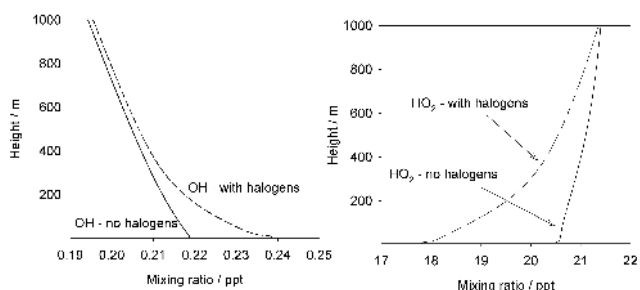


Fig. 6. Vertical profiles of modelled OH and modelled HO₂ at Cape Verde for two scenarios: with and without halogen chemistry. At the height of the measurements, the model scenario without halogen chemistry over-predicts HO₂ by ~14% of the measured mixing ratio, and under-predicts the OH by ~13%. Average observed OH=0.25 pmol mol⁻¹ and HO₂=18 pmol mol⁻¹ (Whalley et al., 2009).

4.5 DMS oxidation

The role of BrO in the oxidation of DMS has been discussed previously (e.g., Toumi, 1994; Saiz-Lopez et al., 2004; von Glasow and Crutzen, 2004; von Glasow et al., 2004). In the tropical MBL, the loss of DMS is thought to take place mainly through oxidation by OH (Turnipseed et al., 1996). However, BrO and to a lesser extent, IO can also cause the oxidation of DMS in the MBL. At the levels of BrO and IO observed at Cape Verde, the oxidation of DMS by BrO is comparable to OH but that by IO is much lower (Table 1). The oxidation of DMS by halogen oxides forms dimethyl sulfoxide (DMSO), which is either rapidly lost to background aerosols or forms methyl sulfinic acid (MSIA) rather than SO₂ and hence H₂SO₄. The presence of halogen oxides would therefore reduce the CCN formation potential of DMS if sulphuric acid formed from OH oxidation were assumed to build up to levels at which it would participate in nucleation (von Glasow and Crutzen, 2004).

4.6 Iodine oxide particle (IOP) formation

There are (at least) two major unresolved questions regarding IOPs: (i) the mechanism whereby iodine oxide molecules polymerize into sub-nm IOPs and (ii) the subsequent growth of these IOPs in the presence of condensable vapours (primarily water and acids) in the marine atmosphere. In the past, the oxidation of iodine oxides by O₃ has been suggested to lead to the formation of I₂O₄ or I₂O₅, which can then polymerise to form IOPs (Jimenez et al., 2003; Saunders and Plane, 2005). However, very recent experiments at the University of Leeds show that IOPs are also produced from IO in the absence of O₃ and hence oxidation of higher iodine oxides by ozone is not a requirement to form IOPs (Saunders et al., 2009). For the present model we have therefore omitted these O₃ reactions. The new work at Leeds indicates that the particles form from the polymerization of

Table 1. Rates of DMS oxidation calculated for observations at Cape Verde. Rates of reactions: OH – Atkinson et al., 2004; IO – Dillon et al., 2006; BrO – Sander et al., 2006.

Radical	Average mixing ratio (pmol mol ⁻¹)	DMS oxidation rate (10 ⁻⁶ s ⁻¹)
OH	0.25	26.4
BrO	2.8	18.4
IO	1.5	0.74

I₂O₃ and I₂O₄, which are produced from the recombination of IO and OIO or the self-association of OIO, respectively (J. C. Gómez Martin, University of Leeds, personal communication, 2009). Quantum calculations, using the same basis set for atomic I described in Kaltsoyannis and Plane (2008), show that I₂O₃ does not dimerize effectively with itself, but forms a much more stable complex with I₂O₄. I₂O₄ also forms a stable dimer with itself. Hence, I₂O₄ appears to be the key species for initiating the formation of IOPs in the MBL. In THAMO, I₂O₄ is treated as the primary polymerising species, on which I₂O₃ can condense. Both species can condense on larger polymers, which can all also coagulate with each other. These reactions are assumed to occur at their respective collision frequencies (or kernels), which is necessary to model the explosive growth of IOPs observed in the laboratory (Saunders and Plane, 2006).

The total number of particles growing to diameter=2 nm are calculated using a semi-implicit, volume conserving coagulation routine as described by Jacobson (2005). Along with growth due to coagulation, I₂O₃, I₂O₄ and IOPs are also lost to background aerosols, the rate of which is calculated according to the molecular transfer approximation (Fuchs, 1964). The THAMO model predicts that I₂O₄ formation is important only during the night at the IO mixing ratios observed at Cape Verde. This is because I₂O₄ forms from the dimerisation of OIO, and OIO photolyzes very rapidly as can be seen in Fig. 4 (Gómez Martin et al., 2009). In the MBL, IOPs can potentially grow much faster due to the uptake of acids and water vapour and there is no reason to expect that condensable vapours in the MBL would not condense onto freshly nucleated particles. Sulphuric acid mixing ratios in the remote MBL range between 0.01–0.03 pmol mol⁻¹ (e.g. Berresheim et al., 1993), and in the presence of sufficient ammonia (NH₃), will condense onto any particles that are formed. Indeed recent laboratory experiments at the University of Leeds show that H₂SO₄ is taken up on humidified IOPs with a mass accommodation coefficient of 0.75 at 90% relative humidity (Saunders et al., 2009). The uptake of H₂SO₄ on ultrafine particles occurs once the particles are large enough to become “activated”; past studies on other atmospheric particles have shown that the activation size ranges between 1.5 and 3 μm (Kulmala et

al., 2007). For simplicity, we do not consider a diurnal profile in the $[\text{H}_2\text{SO}_4]$ and assume that uptake of ammonia (NH_3) will keep the pH of the IOPs close to neutral, so that further uptake of H_2SO_4 is not inhibited. This assumption is valid as the background NH_3 mixing ratio in the MBL ranges between 25 and 75 pmol mol^{-1} (Quinn et al., 1988), and aliphatic amines have been observed in sub- μm particles around Cape Verde (Müller et al., 2009).

Results from the THAMO runs using this IOP formation and growth mechanism are illustrated in Fig. 7. The figure shows the number of particles at the measurement height of 10 m, which might grow large enough (taken to be $>20 \text{ nm}$) to have a good chance of surviving to become CCN. These are the number of potential CCN formed at 10 m after 24 h, as a function of the mean daytime IO concentration at 10 m. The IO is changed by altering the sea-to-air flux of I_2 species in addition to the halocarbon flux as mentioned in Sect. 4.2. Two cases are illustrated in the figure to show the sensitivity to the background aerosol surface area (ASA), which is set to a typical remote MBL value of $1 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$ or an ultra-clean value of $1 \times 10^{-7} \text{ cm}^2 \text{ cm}^{-3}$.

The figure shows that the predicted number of particles is highly sensitive to (i) the background ASA, because the loss to background aerosols through uptake is usually faster than growth by coagulation and condensation (except at high $[\text{IO}]$); and (ii) the IO concentration because the rates of formation of OIO and I_2O_4 depend nonlinearly on $[\text{IO}]$. The figure also demonstrates the probability of forming potential CCN at Cape Verde is vanishingly small. The model predicts a maximum of only $\sim 1 \times 10^{-25}$ particles cm^{-3} (diameter=20 nm) at the height of measurements when the ASA is $1 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$, and $\sim 1 \times 10^{-17}$ when the ASA is $2 \times 10^{-7} \text{ cm}^2 \text{ cm}^{-3}$. Thus, at the mixing ratios of IO seen at Cape Verde, the formation of CCN from iodine chemistry is extremely unlikely. However, the model results show that for a higher $[\text{IO}]$, formation of IOPs could be an important source of new particles in the MBL. Such bursts of new particles (diameter=3–10 nm) have been observed in coastal areas peaking at around 2.5×10^5 particles cm^{-3} (e.g. Whitehead et al., 2009). In these regions $[\text{IO}]$ can reach values as high as $\sim 27 \text{ pmol mol}^{-1}$ (e.g. Whalley et al., 2007). Similar bursts have also been observed in Antarctica, where >4000 particles cm^{-3} were observed in the summer (Davison et al., 1996), when the $[\text{IO}]$ peaks about 10 pmol mol^{-1} (Saiz-Lopez et al., 2007). It should be noted that at the levels of IO observed in Cape Verde, there is little change due to the inclusion of particle formation on the predicted IO mixing ratios because most of the higher oxides are lost via uptake on background aerosol. At higher levels of IO, there would be a significant difference to the flux of iodine necessary to sustain IO, if particle formation is switched off (although this depends on whether the higher oxides undergo reasonably rapid photolysis, as proposed by Saiz-Lopez et al. 2008).

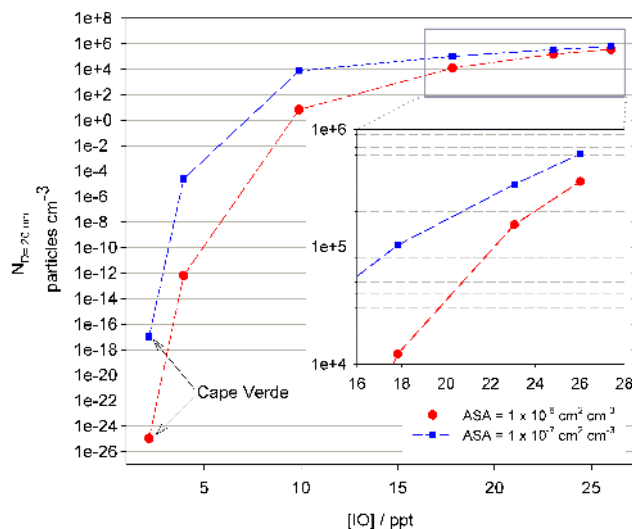


Fig. 7. The number of potential CCN formed at 10 m after 24 h, as a function of the mean daytime IO mixing ratio at 10 m. The $[\text{IO}]$ is changed by altering the sea-to-air flux of I_2 species in addition to the halocarbon flux as mentioned in Sect. 4.2. Two cases are illustrated in the figure to show the sensitivity to the background aerosol surface area (ASA), which is set to a typical remote MBL value of $1 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$ (red) or an ultra-clean value of $1 \times 10^{-7} \text{ cm}^2 \text{ cm}^{-3}$ (blue).

5 Summary and conclusions

Measurements of halogen species at an open ocean site in the tropical Atlantic Ocean are presented. IO and BrO are ubiquitously detected at Cape Verde in the presence of sunlight with no apparent dependence on wind speed or direction. Both radicals display a distinct top-hat profile with the maximum values seen between 09:00–07:00 GMT and the annual profile of both species shows little variation. The presence of IO and BrO above the detection limit of the DOAS instrument indicates that halogen chemistry could play a wide role in the open ocean MBL. Using the 1-D model THAMO, it is shown that the observed iodocarbon fluxes cannot explain the IO measurements, suggesting that other iodine compounds must be emitted from the ocean surface. The modelling results also show that the observed O_3 depletion cannot be explained in the absence of halogen chemistry. The model is able to account for the low HO_x ratio measured at Cape Verde, indicating that halogen chemistry directly affects the oxidising capacity of the atmosphere. Bromine chemistry is shown to oxidise DMS at rates comparable to OH affecting the CCN formation potential of DMS. Finally, modelling results suggest that IOP formation does not occur at Cape Verde and higher IO concentrations are necessary to produce particles of a climatically important size. However, further studies are necessary in order to fully understand the potential of iodine chemistry to form CCN in other open ocean environments.

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