Impact of halogens on global oxidising capacity

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Introduction

Gas phase oxidation processes remove volatile organic compounds (VOCs) from the atmosphere

Atmospheric oxidation is largely controlled by **OH** and **HO_2 - HO_x**

Tropical regions have high HO_x production rates due to high solar irradiance, warmth and humidity
- ⇒ Estimated that ~ 80 % of global CH_4 oxidation occurs in the tropics Bloss *et al.* (2005a)
- ⇒ As much as 25 % of the total global CH_4 oxidation occurs in the tropical marine boundary layer

Cape Verde Atmospheric Observatory (16.85 °N, 24.87 °W), situated on the island of Sao Vicente in the Cape Verde Islands

Understanding tropical HO_x concentrations will lead to better prediction of CH_4 lifetimes and long-term climate trends

HO_x observations were made during the Seasonal Oxidant Study (SOS) in Cape Verde, 2009
- ⇒ Tropical marine Atlantic boundary layer, representative of the open ocean Lee *et al.* (2009)
- ⇒ Measurements during three distinct seasonal periods Vaughan *et al.* (2011)

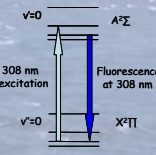
Box and global models used to probe our understanding of OH and HO_2 observations

LIF Detection of OH and HO_2

Radicals detected *in situ* from the roof of a standard shipping container converted into a mobile laboratory Vaughan *et al.* (2011)

Laser induced fluorescence (LIF) detection of OH using Fluorescence Assay by Gas Expansion (FAGE)
- ⇒ Ambient air drawn into low pressure cell (< 4 Torr)
- ⇒ Laser beam passed perpendicular to air stream
- ⇒ On resonance 308 nm OH fluorescence detected by PMT
- ⇒ HO_2 titrated to OH by reaction with NO

	SOS1	SOS2	SOS3
Dates	27th Feb – 8th March	8th – 16th June	1st – 12th Sept
Days of OH HO_2	10	11	10
Average noontime OH	3.82×10^6 cm^{-3}	4.74×10^6 cm^{-3}	4.65×10^6 cm^{-3}
Average noontime HO_2	2.55×10^8 cm^{-3}	2.92×10^8 cm^{-3}	2.88×10^8 cm^{-3}
Average noontime $j(O^1D)$	2.95×10^{-5} s^{-1}	3.48×10^{-5} s^{-1}	3.5×10^{-5} s^{-1}
5-minute LOD OH	3×10^5 cm^{-3}	4×10^5 cm^{-3}	7×10^5 cm^{-3}
4-minute LOD HO_2	7×10^7 cm^{-3}	8×10^7 cm^{-3}	9×10^7 cm^{-3}



Model Approaches

Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) Emmerson & Evans (2009), Stone *et al.* (2010)
- ⇒ Uses the Kinetic Pre-Processor (KPP) Sandu & Sander (2006)
- ⇒ Flexible zero dimensional box model constrained to observations
- ⇒ Photolysis rates calculated from TUV radiation model
- ⇒ Cloud correction factors using observed $j(O^1D)$
- ⇒ Model run forwards to diurnal steady state to calculate OH, HO_2

Chemistry described by the Master Chemical Mechanism (MCM) v3.1
- ⇒ Near explicit degradation schemes
- ⇒ Updated to include chemistry of bromine, iodine and aerosols

Box model calculations limited to observations during Feb-Mar and May-June due to requirements for supporting data

GEOS-Chem Bey *et al.* (2001), Evans & Jacob (2005)
- ⇒ 3D global chemistry transport model v9-01-03
- ⇒ Horizontal resolution of 4° × 5° with 47 vertical levels to 50 hPa
- ⇒ Driven by assimilated winds from Goddard Earth Observing System
- ⇒ Two year model run, analysis using the second year
- ⇒ Run in planeflight mode to give hourly output at the Cape Verde Atmospheric Observatory
- ⇒ Recent model updates include bromine chemistry

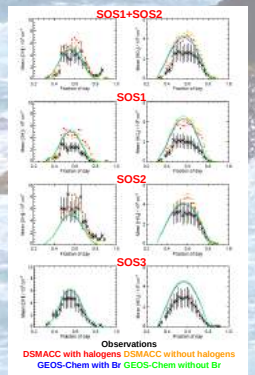
Combination of DSMACC and GEOS-Chem used to assess our understanding of OH and HO_2 in the tropical marine boundary layer

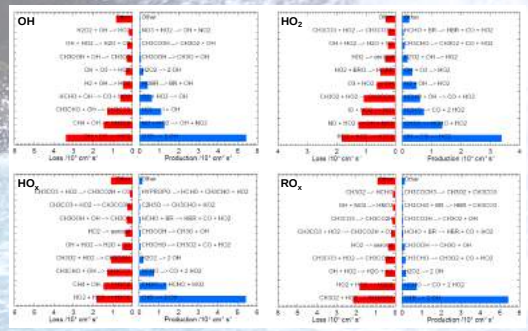
Model Performance

Box model calculations reproduce the observed diurnal variation in OH and HO_2

Simulations tend to overpredict OH and HO_2, particularly for SOS1 (Feb-Mar)

Inclusion of halogen chemistry leads to an increase in modelled OH and a decrease in modelled HO_2 (Noontime BrO = 2.5 ppt; Noontime IO = 1.4 ppt Read *et al.* (2008))





Processes controlling the noontime concentrations of OH, HO_2, HO_x and RO_x in DSMACC

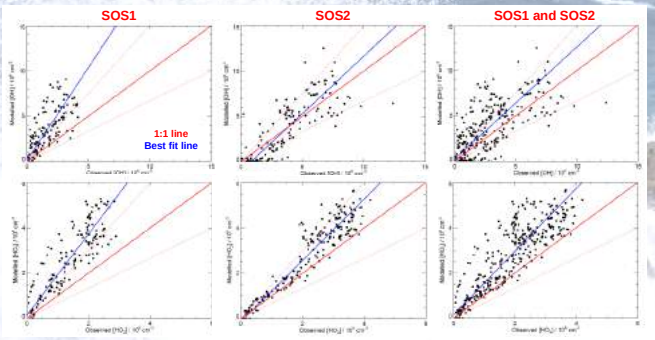
Inclusion of bromine chemistry in global model GEOS-Chem leads to a decrease in both OH and HO_2
- ⇒ Contrast to DSMACC and previous box model studies of the impacts of halogens on HO_x chemistry

e.g. Bloss et al. (2005b), Sommariva et al. (2006), Whalley et al. (2010)

Increased Br emissions in the model lead to further decreases in the modelled OH
- ⇒ Results from BrO catalysed loss of O_3

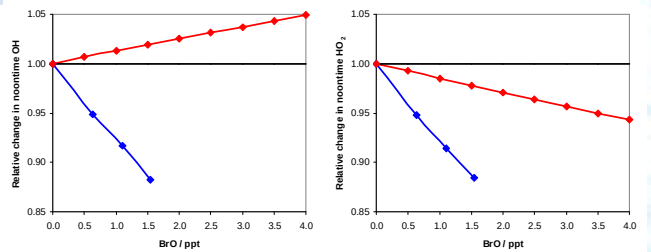
Previous work at the Cape Verde Atmospheric Observatory indicates that BrO and IO cause extensive ozone loss in tropical marine locations Read et al. (2008)

Global impact of halogens on OH and HO_2 could have important consequences for modelling greenhouse gases and understanding climate change



Noontime HO_x production is dominated by ozone photolysis to produce $O(^1D)$ (67 %), $CH_3O + O_2$ (17 %) and photolysis of HCHO (9 %) and H_2O_2 (2.4 %)

Noontime loss of HO_x is controlled by $HO_2 + HO_2$ (22 %), $CH_4 + OH$ (18 %), $CH_3CHO + OH$ (16 %), $CH_3O_2 + HO_2$ (13 %)



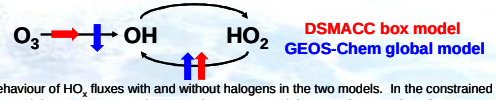
DSMACC box model
GEOS-Chem global model

Relative changes to modelled Cape Verde noontime OH and HO_2 on increasing the concentration of BrO (note that the box model also contains 1.4 ppt IO)

Conclusions

Inclusion of halogens in a global chemistry model leads to a decrease in global OH concentration and a reduction in the global oxidising capacity

Box models constrained to O_3 provide a poor description of the impact of halogens on HO_x chemistry and global oxidising capacity



Behaviour of HO_x fluxes with and without halogens in the two models. In the constrained box model ozone concentrations remain constant and the rate of conversion of HO_2 to OH increases due to BrO, thus OH concentrations increase. In the global model the halogens reduce the O_3 concentration (the primary OH source), but increase the rate of conversion of HO_2 to OH. Overall for OH in the global model the reduction in the primary OH source due to halogens is more significant than the increase in OH due to repartitioning thus OH concentrations decrease.

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