Impact of halogens on global oxidising capacity

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Background

- Gas phase oxidation processes remove volatile organic compounds from the atmosphere
- Atmospheric oxidation largely controlled by **OH** and **HO_2** - **HO_x**
- High solar intensity and warm humid conditions lead to high HO_x production rates in tropical regions

$\Rightarrow$ Estimated that 80 % of global CH_4 oxidation occurs in the tropics

- Measurements at the Cape Verde Atmospheric Observatory have shown significant impacts of halogens on O_3 concentrations
  - Read *et al*., *Nature* 2008, 453, 1232-1235

How does halogen chemistry impact HO_x and the global oxidising capacity?

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This work

- Laser-induced fluorescence observations of OH and HO_2 made during 2009 at the Cape Verde Atmospheric Observatory

  ⇒ Tropical Atlantic marine boundary layer

  ⇒ Representative of the open ocean marine boundary layer

- Model calculations

  ⇒ DSMACC box model

  ⇒ GEOS-Chem global model

Can we understand the observations?
What is the impact of halogen chemistry?

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Model Approaches

- **DSMACC** Dynamically Simple Model of Atmospheric Chemical Complexity
- Flexible zero-dimensional box model constrained to observations
- Chemistry scheme described by the Master Chemical Mechanism (MCM) with updates for bromine, iodine and aerosol chemistry
- Model run forwards to diurnal steady state

- **GEOS-Chem** v9-01-03, 4 5 resolution
- Two year model runs for 2009, analysis using the second year
- Run in planeflight mode to give hourly output at the Cape Verde Atmospheric Observatory
- Includes recent bromine chemistry updates

How do the box model calculations compare to the global model?

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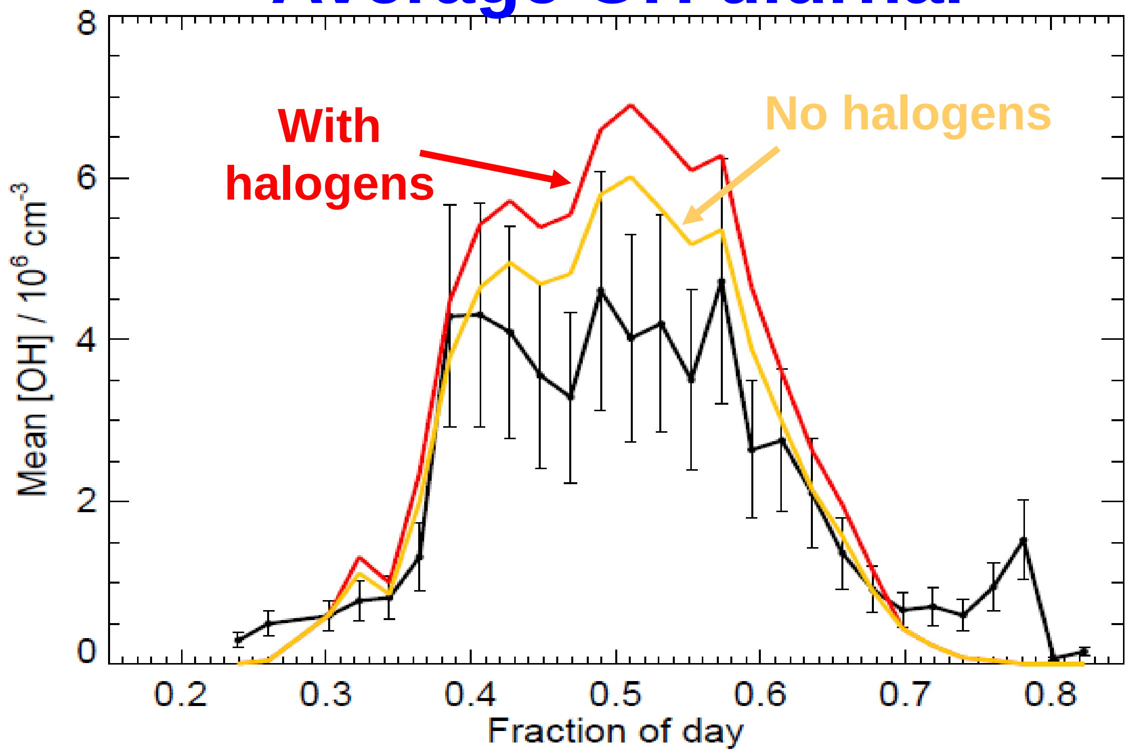
DSMACC Model Performance

- Box model calculations reproduce the observed diurnal variation but tend to overpredict the observations

Average OH diurnal



Inclusion of halogen chemistry in the box model leads to increased OH

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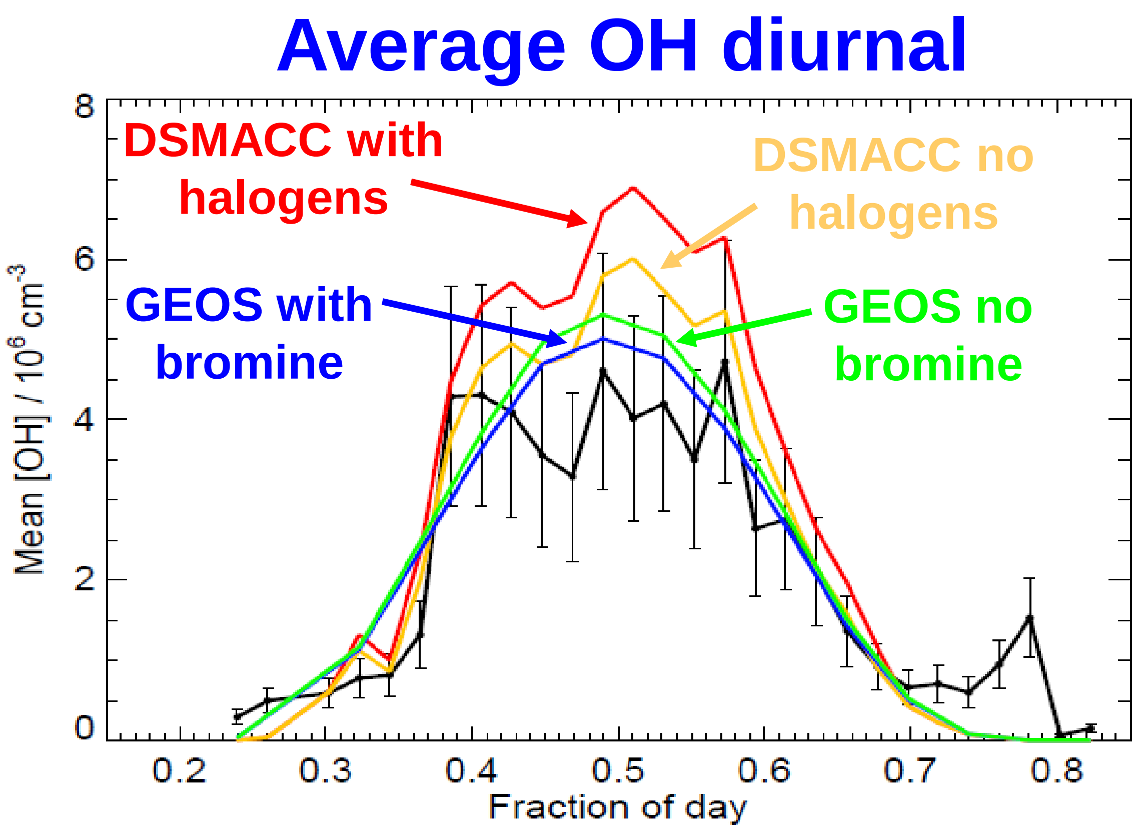
GEOS-Chem Model Performance



Inclusion of Br chemistry in the GEOS-Chem model leads to decreased OH

Effects of Br in contrast to DSMACC

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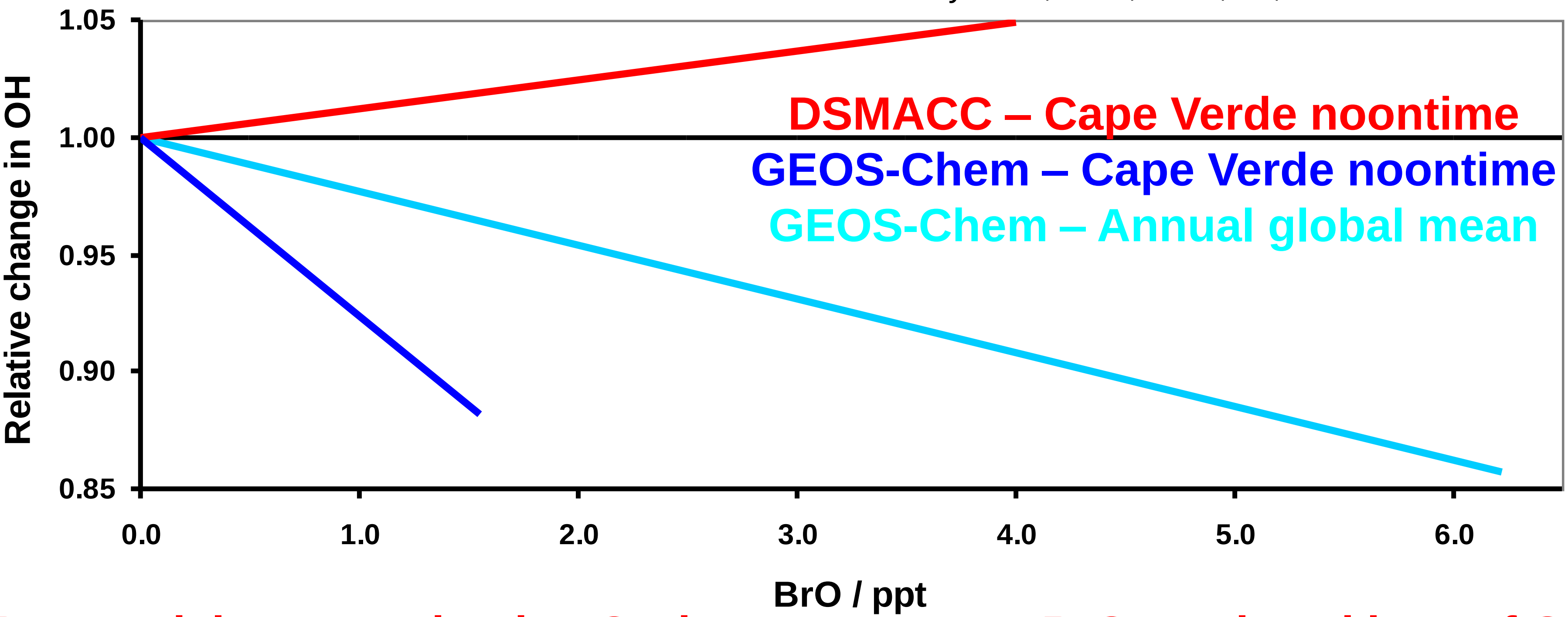
Impacts of halogens on OH

- Inclusion of Br chemistry in GEOS-Chem leads to a decrease in OH
- Contrast with DSMACC and previous box model studies of the impacts of halogens on HO_x chemistry

Bloss *et al*., *Geophys. Res. Lett.*, 2005, 32, L06814
Sommariva *et al*., *ACP*, 2006, 6, 1135-1153
Whalley *et al*., *ACP*, 2010, 10, 1555-1576



Box models constrained to O_3 do not represent BrO catalysed loss of O_3

Needs to be considered when assessing impacts of halogens on HO_x

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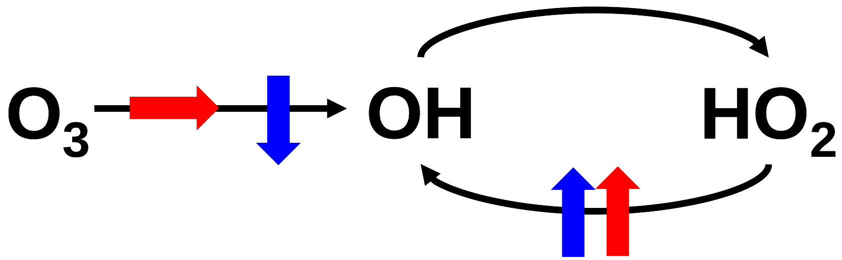
Conclusions

- 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



DSMACC box model
GEOS-Chem global model

DSMACC: O_3 constant, BrO converts HO_2 to OH $\Rightarrow$ more OH

GEOS-Chem: O_3 decreases, reduction in primary OH source outweighs conversion of HO_2 to OH $\Rightarrow$ less OH

Annual mean 4 ppt BrO leads to 9 % reduction in OH and 11 % increase in methane lifetime

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Acknowledgements

Stewart Vaughan
Trevor Ingham
Lisa Whalley

Bruno Faria
Luis Mendes
Gisela Duarte

James Lee
Katie Read
Sarah Moller
Lucy Carpenter

Justin Parrella
Daniel Jacob

NERC
NCAS

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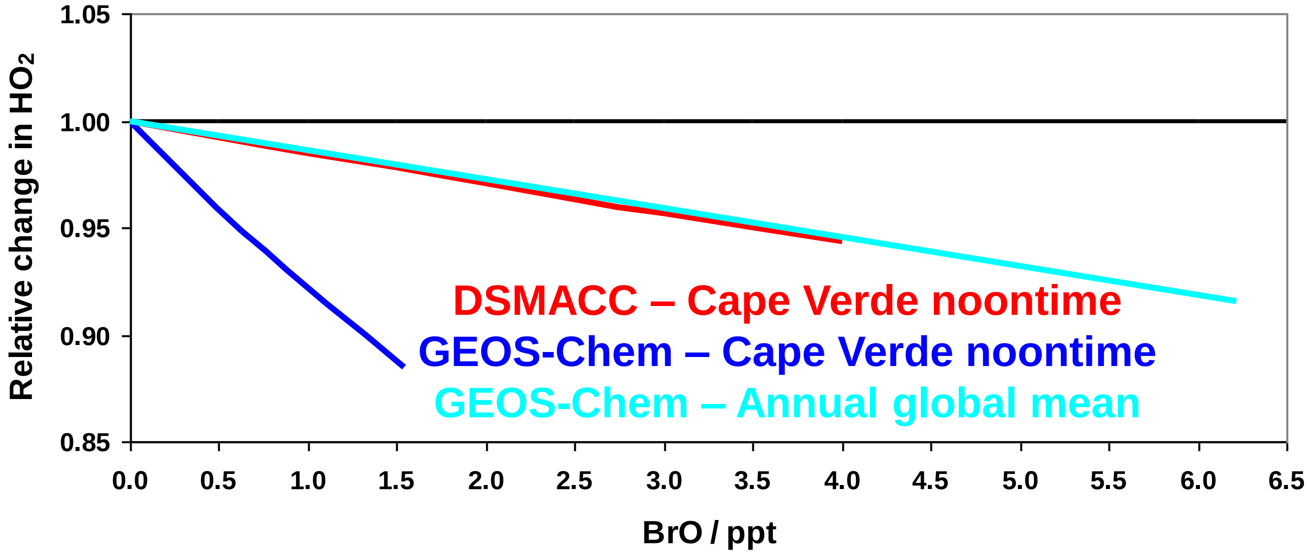
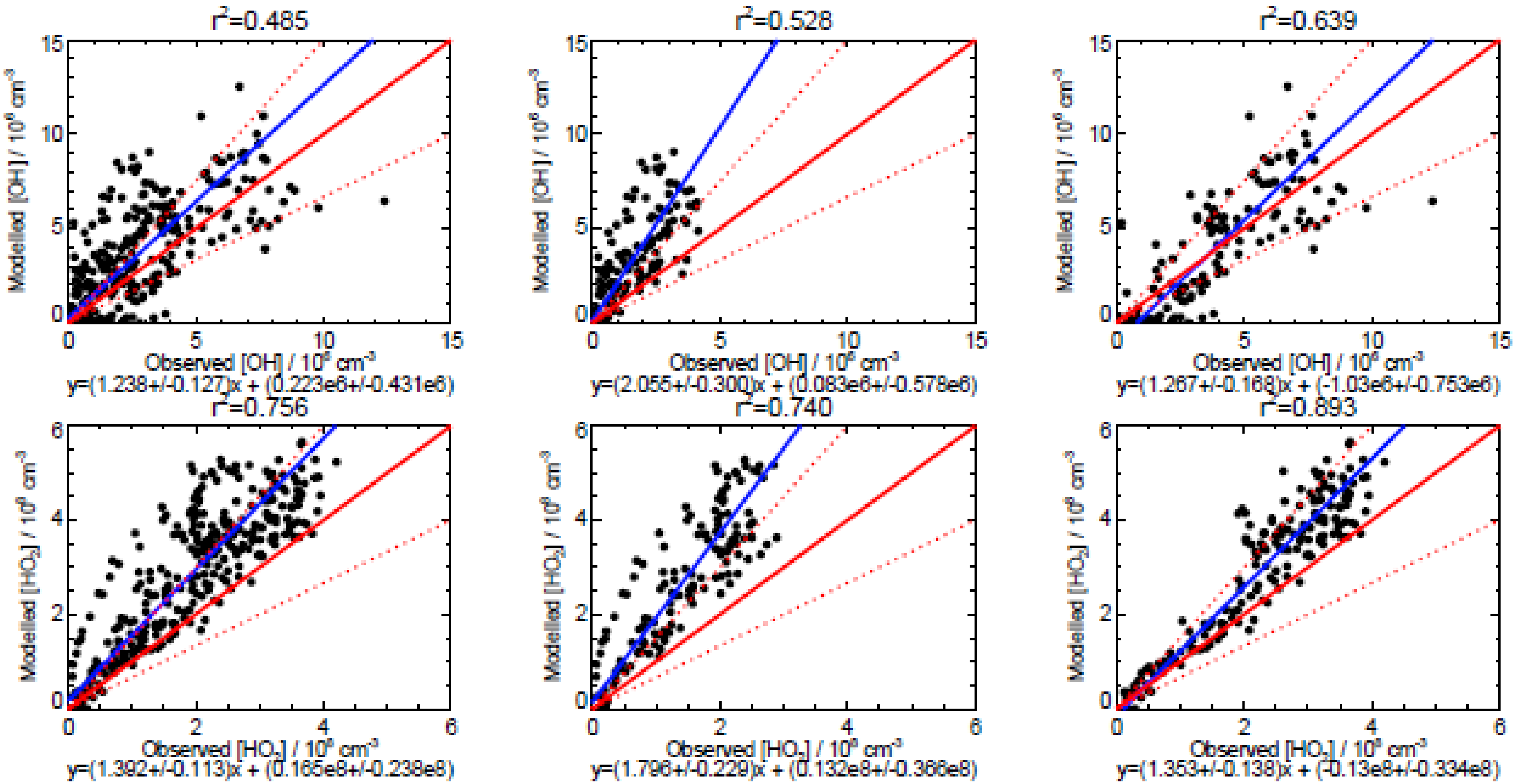


Relative change in HO_2
1.05
1.00
0.95
0.90
0.85
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
BrO / ppt
DSMACC – Cape Verde noontime
GEOS-Chem – Cape Verde noontime
GEOS-Chem – Annual global mean



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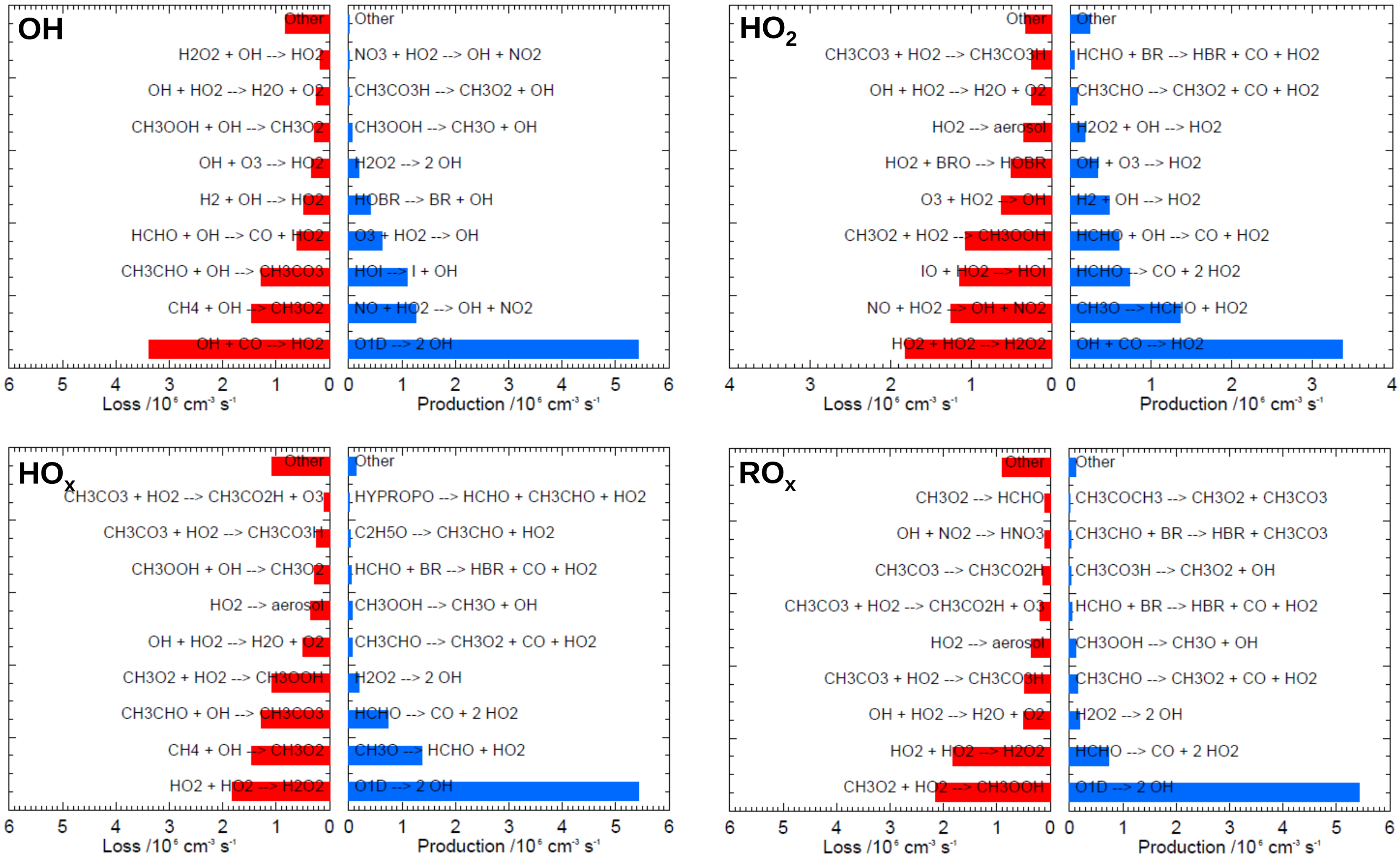
Processes controlling OH and HO_2



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

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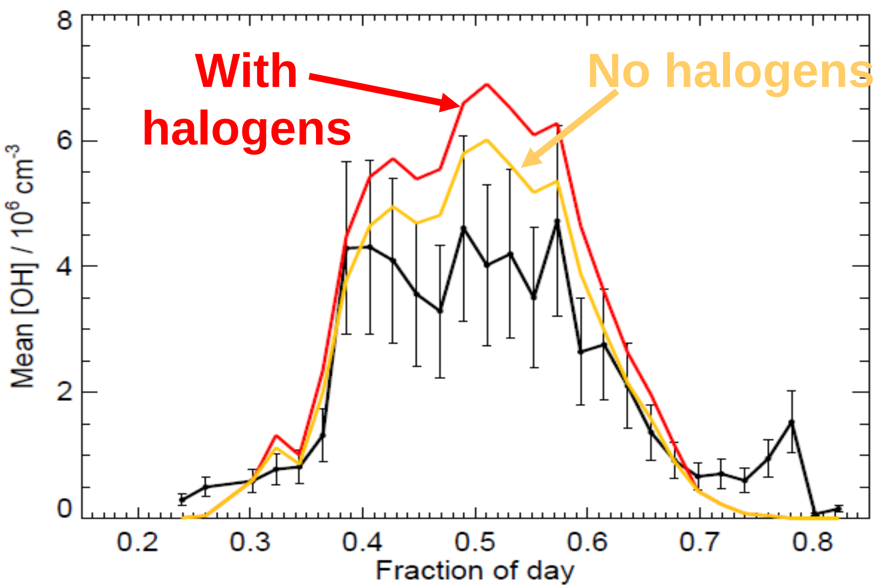
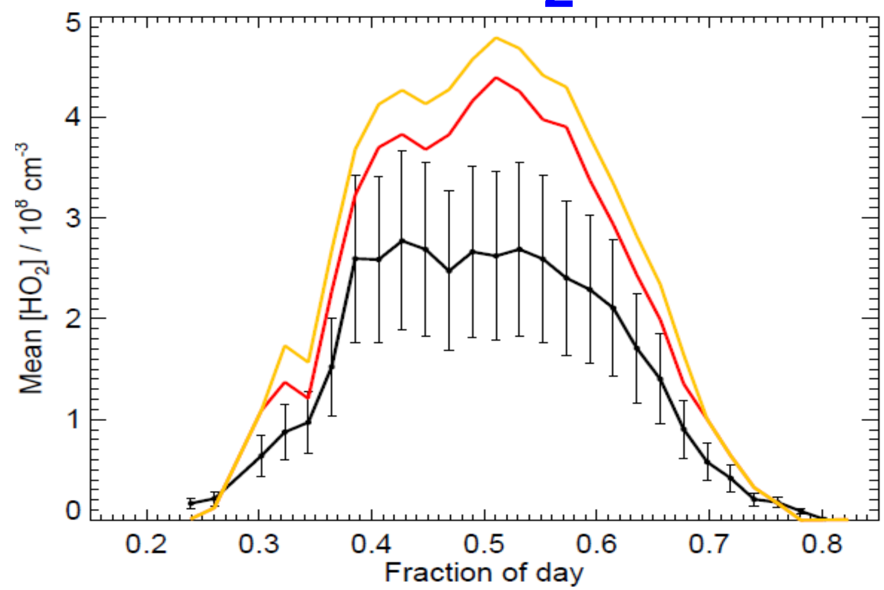
DSMACC Model Performance

- Box model calculations reproduce the observed diurnal variation in OH and HO_2
- Simulations tend to overpredict HO_x observations

OH



HO_2



Inclusion of halogen chemistry in the box model leads to increased OH and decreased HO_2

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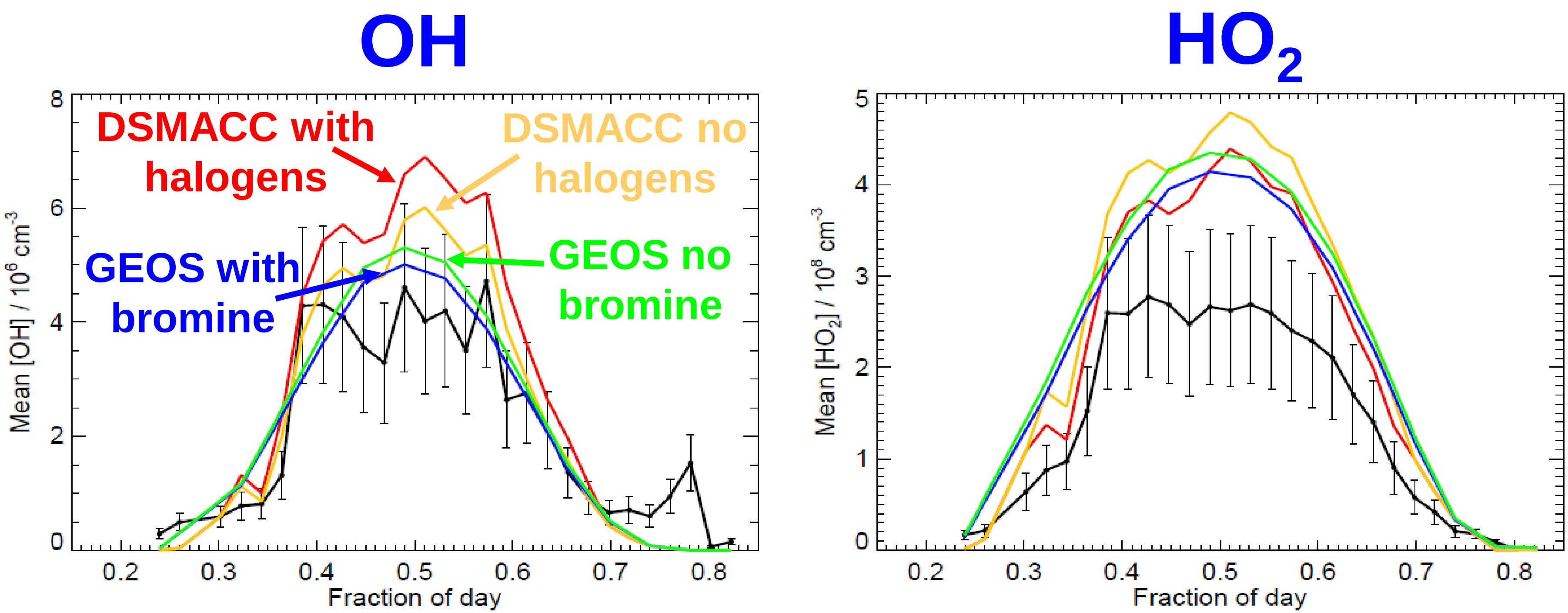
GEOS-Chem Model Performance



Inclusion of Br chemistry in the GEOS-Chem model leads to decreased OH

Effects of Br in contrast to DSMACC

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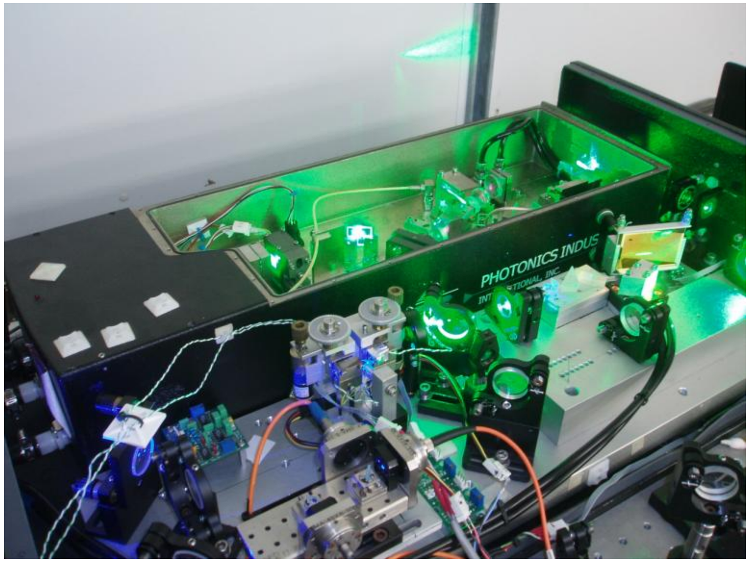
Measuring OH and HO_2

- **F**luorescence **A**ssay by **G**as **E**xpansion
- **L**aser **I**nduced **F**luorescence
- Ambient air drawn into low pressure detection cell (< 1 Torr)
- Laser beam passed across gas beam



- On-resonance fluorescence of OH radicals
- Fluorescence signal detected at PMT
- HO_2 detection by chemical titration to OH

$$HO_2 + NO \rightarrow OH + NO_2$$

DSMACC Box Model

- **D**ynamically **S**imple **M**odel of **A**tmospheric **C**hemical **C**omplexity
  - Emmerson & Evans, *ACP* 2009, 9, 1831-1845, Stone *et al*., *ACP* 2010, 10, 9415-9429
- Uses the Kinetic Pre-Processor (KPP)
  - Sandu & Sander, *ACP* 2006, 6, 187-195
- Flexible zero dimensional box model constrained to observations
- Photolysis rates calculated by TUV radiation model
- Cloud correction factors using observed $j(O^1D)$
- Model run forwards to diurnal steady state

- Chemistry described by the Master Chemical Mechanism, updated to include bromine, iodine and aerosol chemistry

GEOS-Chem Global Model

- 3D global chemistry transport model v9-01-03
- Horizontal resolution of 4^{o} 5^{o} with 47 vertical levels up to 50 hPa
- Two year model run for 2009, with analysis using the second year
- Run in planeflight mode to give hourly output at the Cape Verde Atmospheric Observatory
- Includes recent updates to include bromine chemistry

	SOS1	SOS2	SOS3
Dates	27th Feb – 8th March	6th – 16th June	1st – 15th 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	2.16×10^8 cm^{-3}	2.92×10^8 cm^{-3}	2.88×10^8 cm^{-3}
Average noontime $j(O^1D)$	2.66×10^{-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	7×10^5 cm^{-3}	9×10^5 cm^{-3}	9×10^5 cm^{-3}