Global modelling of iodine in the troposphere and lowermost stratosphere

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1. Motivation
2. Implementation of VSL halogenated sources in CAM-Chem
3. Model results for reactive bromine / iodine
4. Impact of bromine / iodine on $O_3$ (tropics)
5. Summary and ongoing work
Halogen chemistry has a significant and extensive influence on photochemical ozone loss in the tropical Atlantic Ocean boundary layer (Read et al., Nature, 2008).

### 1. Motivation

**1. Troposphere**

- Observations of IO, BrO, etc. in polar and coastal areas
- Presence of IO and BrO confirmed over the open oceans

**Scientific questions:**
- Impact of halogens on the $O_3$ budget
- Impact on $HO_x$, $NO_x$, methane lifetime

Halogen chemistry has a significant and extensive influence on photochemical ozone loss in the tropical Atlantic Ocean boundary layer (Read et al., Nature, 2008).

**IO and BrO at ppt levels**

(Saiz-Lopez et al., ACP, 2012)
1. Motivation

Solomon et al., JGR, 1994
Gilles et al., JPC-A, 1997

“Iy = 1 pptv”

“On the role of iodine in ozone depletion”, Solomon et al., JGR, 1994

Since then:

- New kinetic information on iodine available
- Attempts to detect reactive iodine in the UTLS
  
  Wennberg et al., JGR, 1997
  Wittrock et al., GRL, 2000
  Wittrock et al., GRL, 2000
  Bösch et al., JGR, 2003
  Butz et al., ACP, 2009

Most recent analyses:

- \( \leq 0.1 \) pptv \( \text{IO, OIO} \) in lower stratosphere
  (in northern high and mid-latitudes, and tropics)

- Estimated total inorganic iodine:
  \( I_y \sim 0.2 \) pptv
  (Photochemical 1-D model)


Unlikely that iodine plays a significant role in the
photochemistry of stratospheric ozone
2. Implementation of VSL sources

CAM-Chem

- Fixed SST and ice (monthly climatology)
- 1.9° (lat) x 2.5° (lon) horizontal resolution
- 26 vertical levels (surface to ~4 hPa)
- Tropospheric and stratospheric chemistry (Emmons et al., 2010; Kinnison et al., 2007)

VSL Halogen Chemistry

- Implementation of VSL (τ < 6 months) halogenated sources from the ocean

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(Bell et al., 2002)
2. Implementation of VSL sources

CAM-Chem
- Fixed SST and ice (monthly climatology)
- 1.9° (lat) x 2.5° (lon) horizontal resolution
- 26 vertical levels (surface to ~ 4 hPa)
- Tropospheric and stratospheric chemistry (Emmons et al., 2010; Kinnison et al., 2007)

VSL Halogen Chemistry
- Implementation of VSL ($\tau < 6$ months) halogenated sources from the ocean
- Emissions following Chl-a over tropics
- Top-down approach (following Warwick et al., JGR, 2006; Liang et al., ACP, 2010)
- Photochemistry
- Dry / wet deposition
- Catalytic release from sea-salt

Ordóñez et al., ACP, 2012 → Description and evaluation of VSL sources
3. Results: Daytime bromine profiles over the tropical oceans

Notes:

- SLIMCAT run with CH₃Br (9.6 ppt), halons (6.8 ppt), and VSLS (4 ppt as CH₂Br₂) plus PGs (1 ppt as HBr).

- Photochemical breakdown only in stratosphere.

Notes CAM-Chem:

- Halons = H-1211 + H-1301 (i.e. CF₂ClBr + CF₃Br)
- VSLS = 3 CHBr₃ + 2 CH₂Br₂ + CH₃BrCl + 2 CHBr₂Cl + CHBrCl₂
- Total Brₓ = Br + BrO + HBr + BrONO₂ + BrCl + HOBr
Iy = I + IO + OIO + IONO2 + HI + HOI

Daytime profiles in tropics

~0.1 ppt Iy enters the stratosphere

~0.20 ppt Iy at 15 km

~0.1 ppt CH3I enters the TTL

Smallest dissociation rate of I2O2 over tropics

Iy = I + IO + OIO + IONO2 + HI + HOI

Butz et al. (2009): Upper limits of IO, OIO ~ 0.1 ppt
Iodine partitioning in LMS (thermal tropopause – 400 K isentrope)

- $\text{I}_2\text{O}_4$
- $\text{I}_2\text{O}_2$
- HOI
- HI
- IONO$_2$
- INO$_2$
- OIO
- I
- IO
- CH$_3$I

$\sim 0.1$ ppt

- $\text{I}_2\text{O}_4$
- $\text{I}_2\text{O}_2$

$\sim 1$ ppt

BrO $> \text{Br}$

IO $< \text{I}$
4. Halogen-driven ozone loss in the tropics (VSL *minus* no VSL)

**Change in tropical tropospheric ozone column:**

\[ \Delta O_3 = -2.6 \text{ DU (10.5 %)} \]

\[ \Delta O_3 = -0.8 \text{ DU (3.2%)} \]

\[ \Delta O_3 = -1.8 \text{ DU (7.3%)} \]

*Yang et al., JGR, 2005:*

4-6% trop. O$_3$ loss
(due to bromine)

*Parrella et al., ACPD, 2012:*

6.5 % trop. O$_3$ loss
(due to bromine)
Annual average difference in radiation fluxes at tropopause

**Longwave flux (W m\(^{-2}\))**
- All-sky: -0.104
- Clear-sky: -0.138

**Net flux (W m\(^{-2}\))**
- All-sky: -0.103
- Clear-sky: -0.122

**VSL - base run**

**Sensitivity under all-sky conditions:**
\[ \frac{0.10 \text{ W m}^{-2}}{2.5 \text{ DU}} = \frac{0.04 \text{ W m}^{-2}}{\text{DU}} \approx \frac{0.042 \text{ W m}^{-2}}{\text{DU}} \]
(Ramaswamy et al., IPCC, 2001)

**Average for tropics (20° S – 20° N)**

**Latitude (°)**

**Is our -0.100 Wm\(^{-2}\) significant?**

**LWRE from tropospheric ozone:**
- All-sky: \(~ 0.33 \text{ W m}^{-2}\)
- Clear-sky: \(~ 0.50 \text{ W m}^{-2}\)

This negative contribution is \(~ 30\%\) of the positive contribution to the TOA radiation flux associated with infrared ozone absorption.

(Ramawat et al., ACP, 2012)
Sensitivity runs: photolysis of $I_2O_y$

High levels of $I_2O_2$, $I_2O_3$, $I_2O_4$

Ozone depletion efficiency by iodine enhanced if $I_2O_y$ photolysis is included.

However significant uncertainties:

- $I_2O_y$ absorption cross sections
- Possible mechanism for iodine loss (e.g. uptake by stratospheric aerosols)
5. Summary & ongoing work

- **VSL** oceanic sources and chemistry of bromine/iodine implemented in **CAM-Chem 3.6.x**
  - Current work: Implementation in **CESM 1.1**

- **Iodine partitioning**: high I/IO ratio in tropical UTLS

- **Iodine-mediated ozone depletion**, compared to bromine, dominates throughout the tropical troposphere (impact on TOA radiation flux), but small in tropical LMS.

- Experimental work on $I_2O_y$ (and other iodine species) is key to further determine the role of iodine in ozone depletion in the UTLS
1. Motivation
2. Stratosphere

Since then:

- New kinetic information on iodine available
- Attempts to detect reactive iodine in the UTLS

**Sci. Assessment of Ozone Depletion (WMO, 2011):**

- Unlikely that iodine plays a significant role in the photochem. of stratospheric ozone
- VSLS contribute to stratospheric bromine ~1–8 ppt.
- Uncertainties in quantifying the impact of Cl- and Br-containing VSLS on stratospheric ozone
- Contribution of VSLS to stratosphere could be altered under a changed climate

3. CESM framework
 Feedbacks among the different elements in the climate system
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Very short-lived halogens
($\tau < 6$ months, WMO)

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\[ \text{NO}_2 \rightarrow \text{XONO}_2 \]
\[ \text{HO}_2 \rightarrow \text{HOX} \quad \text{hu} \rightarrow \text{OH} + X \]
\[ \text{XO} \rightarrow \text{OXO} + X \]
\[ \text{X} \quad X = \text{Cl, Br or I} \]

\[ \text{IO} \rightarrow \text{I}_2 \text{O}_2 \]

\[ \text{O}_3 \quad \text{hu} \rightarrow \text{OH} \]

\[ \text{h}_\nu \rightarrow \text{X} \quad \text{X = Cl, Br or I} \]
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\( X = \text{Cl, Br or I} \)

\( \text{NO}_2 \rightarrow \text{XONO}_2 \)

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\( \text{O}_3 \rightarrow \text{IO} \rightarrow \text{I}_2\text{O}_2 \)

\( \text{OH} \rightarrow \text{O}_3 \)

\( h\nu \rightarrow \text{X} \rightarrow \text{XO} \)

\( \text{XO} \rightarrow \text{O}_x \text{O} \rightarrow \text{X} \)

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**Very short-lived halogens**

($\tau < 6$ months, WMO)

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**Chemical Reactions**

- $\text{NO}_2 \rightarrow \text{XONO}_2$
- $\text{HO}_2 \rightarrow \text{HOX} \rightarrow \text{OH} + \text{X}$
- $\text{XO} (\text{X} = \text{Br, I, Cl}) \rightarrow \text{OXO} + \text{X}$
- $\text{O}_3 \rightarrow \text{X}$
- $\text{X} = \text{Cl, Br or I}$
- $\text{XO}_2$
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**Very short-lived halogens**  
(\( \tau < 6 \) months, WMO)

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Introductory conclusion: Oxidizing capacity and \( O_3 \) radiative impact
Example: CHBr$_3$ emissions

Ordóñez et al., ACP, 2012
Comparison with aircraft observations (1996 – 2008)

Troposphere
(1000 – 200 hPa)

UTLS (300 – 50 hPa)

Comparison with monthly output from the latest year of a model simulation
Bromoform (CHBr₃)

aircraft (mean ± stdev)

model (mean ± stdev)
Bromoform (CHBr₃)

aeroplanes (mean ± stdev)

model (mean ± stdev)
Dibromomethane ($\text{CH}_2\text{Br}_2$)

![Graphs showing the distribution of dibromomethane across different models and aircraft measurements.](image)
150 – 70 hPa: Overestimation of obs by ~70%

Similar result in previous studies

Potential reasons:
Uncertainty in $k(\text{CH}_2\text{Br}_2 + \text{OH})$, etc.
Underestimation of CH$_3$I, and possibly of O$_3$ loss by iodine chemistry in the UTLS

For more on:
- Evaluation of VSLS (Ordóñez et al., ACP, 2012)
- Impact of VSLS on the Earth’s radiative balance through their effect on tropospheric O3 (Saiz-Lopez et al., ACP, 2012)
4. Halogen-driven ozone loss in troposphere (VSL *minus* no VSL)

Troposphere (200 hPa – surface):  
max  mean  min  
-5.0  -3.0  -1.0  DU  

~ 9% of trop. column

Yang et al., JGR, 2005:  
4-6% trop. O$_3$ loss  
(due to bromine)

Parrella et al., ACPD, 2012:  
6.5 % trop. O$_3$ loss  
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4. Halogen-driven ozone loss in troposphere (VSL minus no VSL)

Yang et al., JGR, 2005: 4-6% trop. O₃ loss (due to bromine)

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Troposphere (200 hPa – surface):
max mean min
-5.0 -3.0 -1.0 DU

~ 9% of trop. column

LT (surface – 850 hPa):
max mean min
-1.0 -0.5 -0.0

17%

No ice emissions

FT (850 hPa – 200 hPa):
max mean min
-4.6 -2.5 -1.0

83%
Ozone loss: Br / I contribution to trop. column - Global
Ozone loss: Br / I contribution to trop. column - Global

Cl + Br + I  Bromine  Iodine

Tot 44%  Tot 56%

LT  FT
Ozone loss: Br / I contribution to trop. column - **Global**

- **Cl + Br + I**
  - Bromine: Tot 44%, LT 7%, FT 37%
  - Iodine: Tot 56%

Check TROPAUSE LEVEL
Ozone loss: Br / I contribution to trop. column - Global

Cl + Br + I

Bromine:
- Tot: 44%
- LT: 7%
- FT: 37%

Iodine:
- Tot: 56%
- LT: 8%
- FT: 48%
Ozone loss: Br / I contribution to trop. column - Tropics

Cl + Br + I

Bromine

Tot 44% 30%
BL 7% 8%
FT 37% 22%

Iodine

Tot 56% 70%
BL 8% 10%
FT 48% 60%
Annually-globally integrated O$_3$ column difference (tropopause + 2 km above) VSL minus no VSL

- Globally, additional O$_3$ loss from Br and I:
  - VSL Br contrib. to O$_3$ loss: ~65%
  - I contrib. to O$_3$ loss: ~34% (but I contributes more than Br over the tropics)

Up to ~1.7 DU O$_3$ loss

Avg. O$_3$ loss by VSLS: 3.5% (range 2-8%)

Ozone loss: Br / I contribution to LMS
1. Motivation

VSL minus base run
1. Motivation

VSL bromine *minus* base run

Iodine *minus* base run

![Graphs showing O change in percent between iodine base runs](image)
(VSL + IONO2 uptake) minus base run (VSL + IONO2 uptake + I2Oy photol)
I2Oy photol

![Graph showing changes in iodine isotope ratio](image)
1. Motivation