Modelling of reactive halogens in the marine atmosphere

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Acknowledgements: Roberto Sommariva, now Univ Leicester

COAS
Centre for Ocean and Atmospheric Sciences

- Established at UEA in Aug 2013 uniting ocean and atmospheric sciences; physics, chemistry and biology
- Unique portfolio of research and facilities
- ~32 faculty members, ~100 fellows, postdocs, PhD students, technicians
- Main objectives:
  - To form a nationally and internationally **known and recognised centre of excellence** in the fields of atmosphere and ocean science, comprising physical, chemical and biological elements
  - To **strengthen existing strategic partnerships**
  - To **intensify and develop international collaborations**
- Director: Prof Roland von Glasow, Deputy: Prof Karen Heywood
- Mainly School of Environmental Sciences but also Schools of Mathematics and Biology

Overview

- ~~Halogens - Why do we care?~~
- Past modelling work: Cape Verde
- Open questions
- New project: “Importance of Marine Gases and Particles for Tropospheric Chemistry” (IGAP)

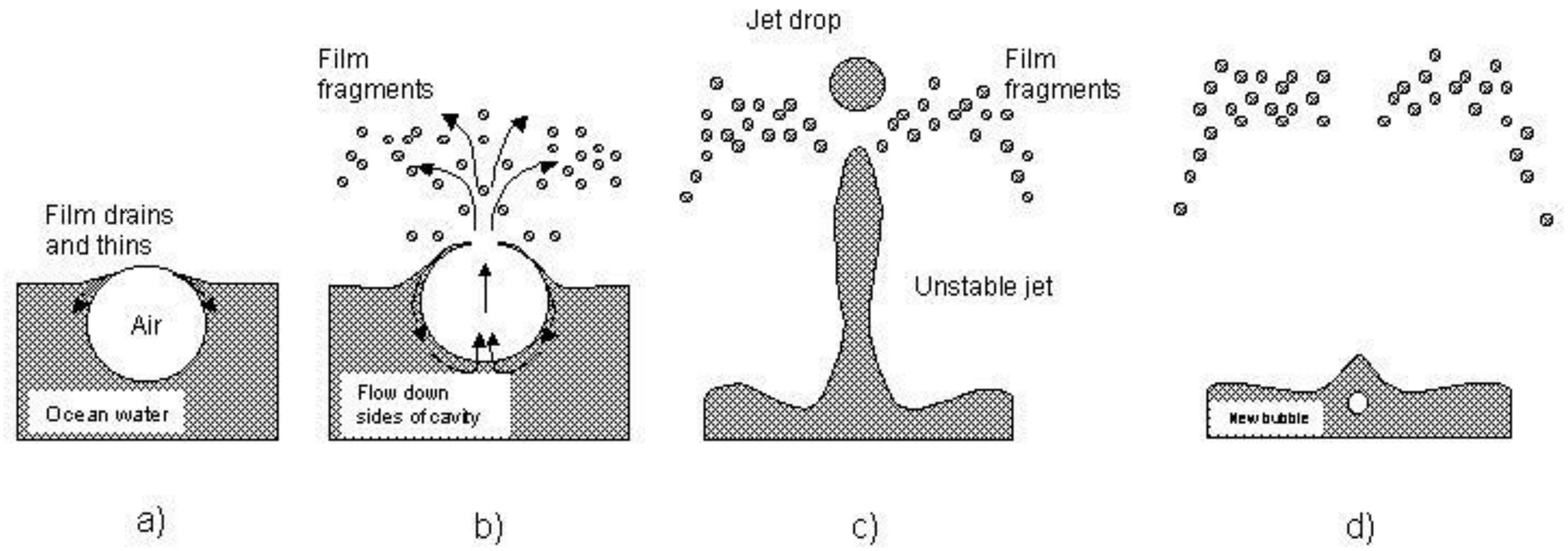
Sources for halogen in marine troposphere

- Bromine, chlorine
  - Sea salt aerosol
    - Photochemical release
    - Acid displacement (HCl only)
  - Organic precursors (e.g. $CHBr_3$, τ ~ weeks - months)
- Iodine
  - Organic precursors (e.g. CH_2I_2, τ ~ mins - days)
  - Inorganic precursors (HOI, I_2, τ ~ 10s sec - mins)
  - Aerosol is *sink*
- Vast majority of sources is natural

Sea salt aerosol - halogens

production of sea salt aerosol:

bubble bursting



fresh sea salt contains:

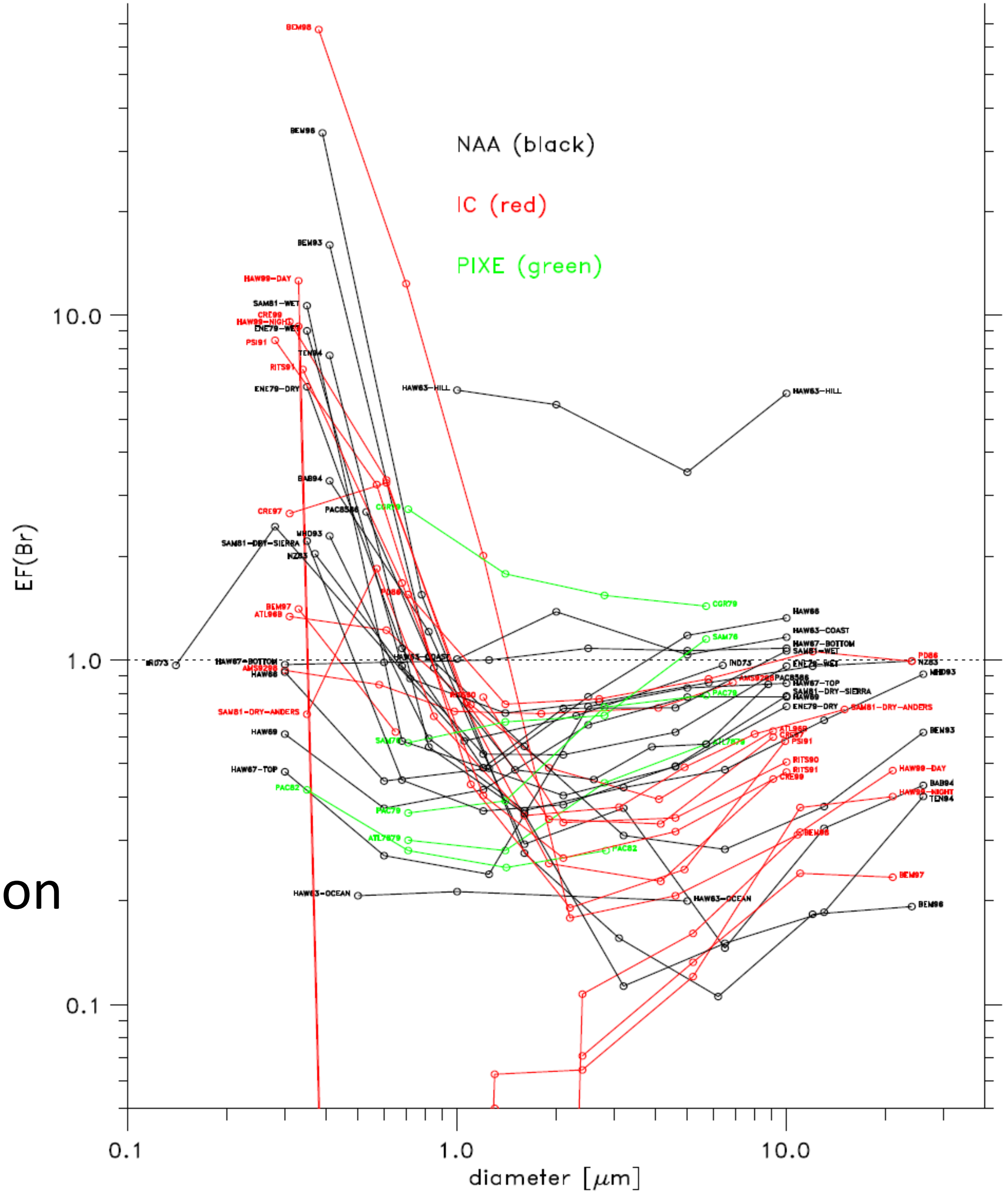
Na^+, Cl^-, Br^-, HCO_3^-, SO_4^{2-},
DOC, POC..

Bromide deficit in marine aerosol

- filter measurements show Br^- deficit in most particles with $d>0.6\mu m$
- enrichment factor:

$$EF = \frac{Br^- : Na^+ \big|_{aerosol}}{Br^- : Na^+ \big|_{seawater}}$$

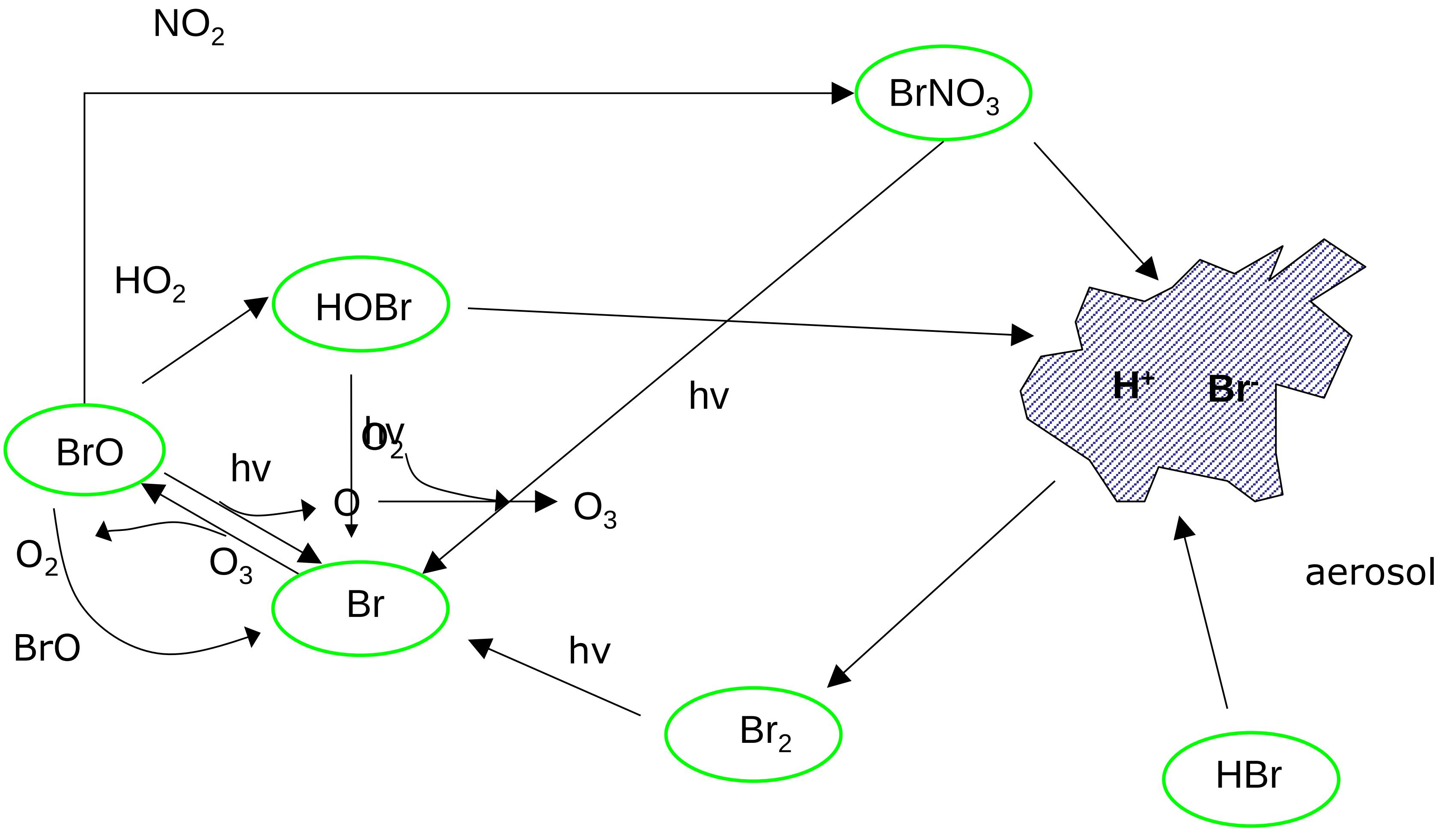
$EF < 1 \Rightarrow Br^-$ deficit



average “by eye”: 50% depletion

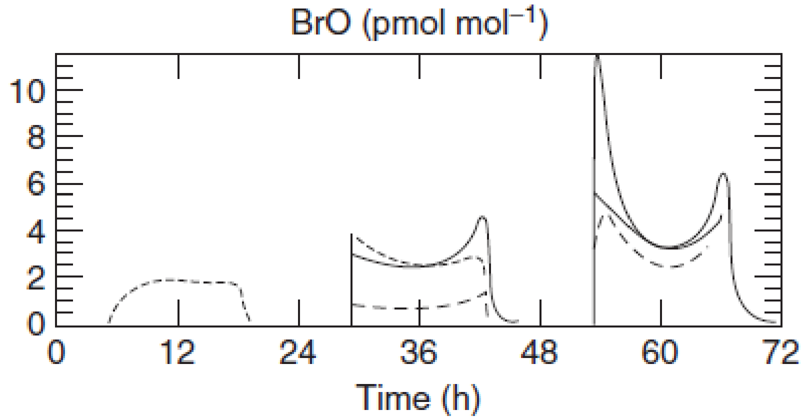
Sander et al., 2003

"Bromine explosion"

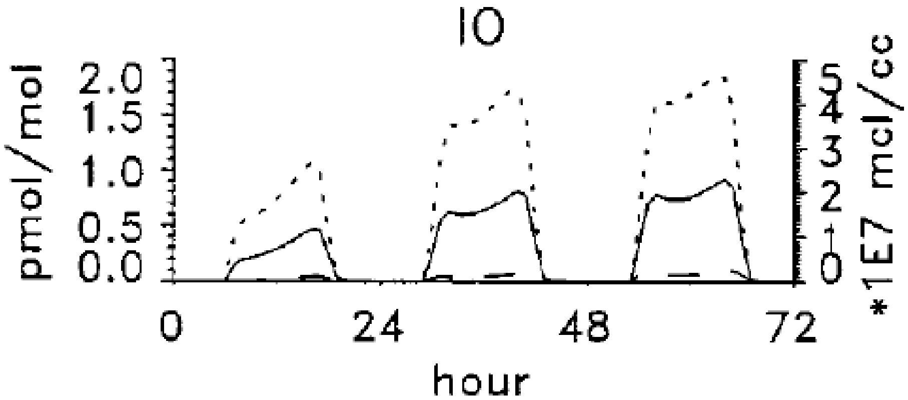


Early(-ish) model studies

- Fan and Jacob, 1992: “Bromine explosion” mechanism can lead to rapid release of bromine in Arctic
- Sander and Crutzen, 1996: Polluted MBL
- Vogt et al., 1996: Clean MBL, further Br – Cl couplings
- Vogt et al, 1999: iodine chemistry
- von Glasow et al., 2002a: distinct diurnal variation and vertical profile, importance for sulphur cycle, sunrise ozone destruction, …

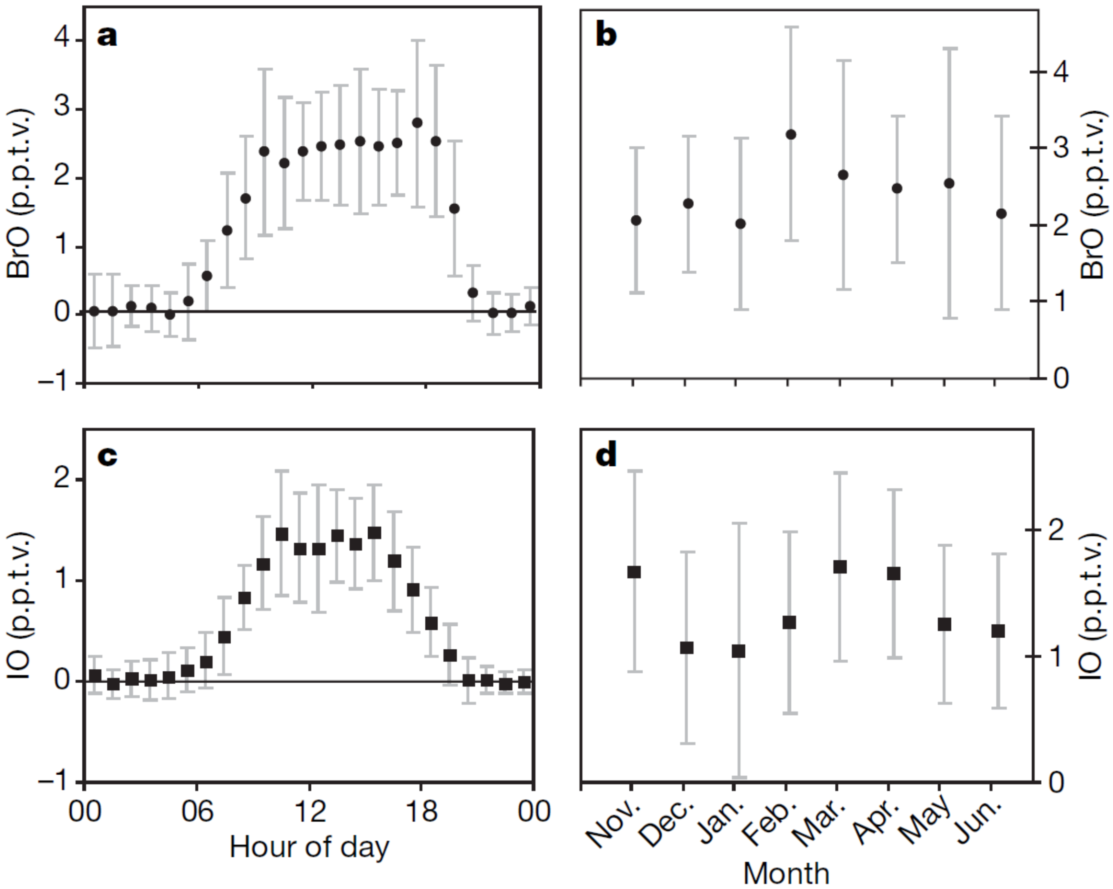


von Glasow et al., 2002a



Vogt et al., 1999

BrO and IO at Cape Verde



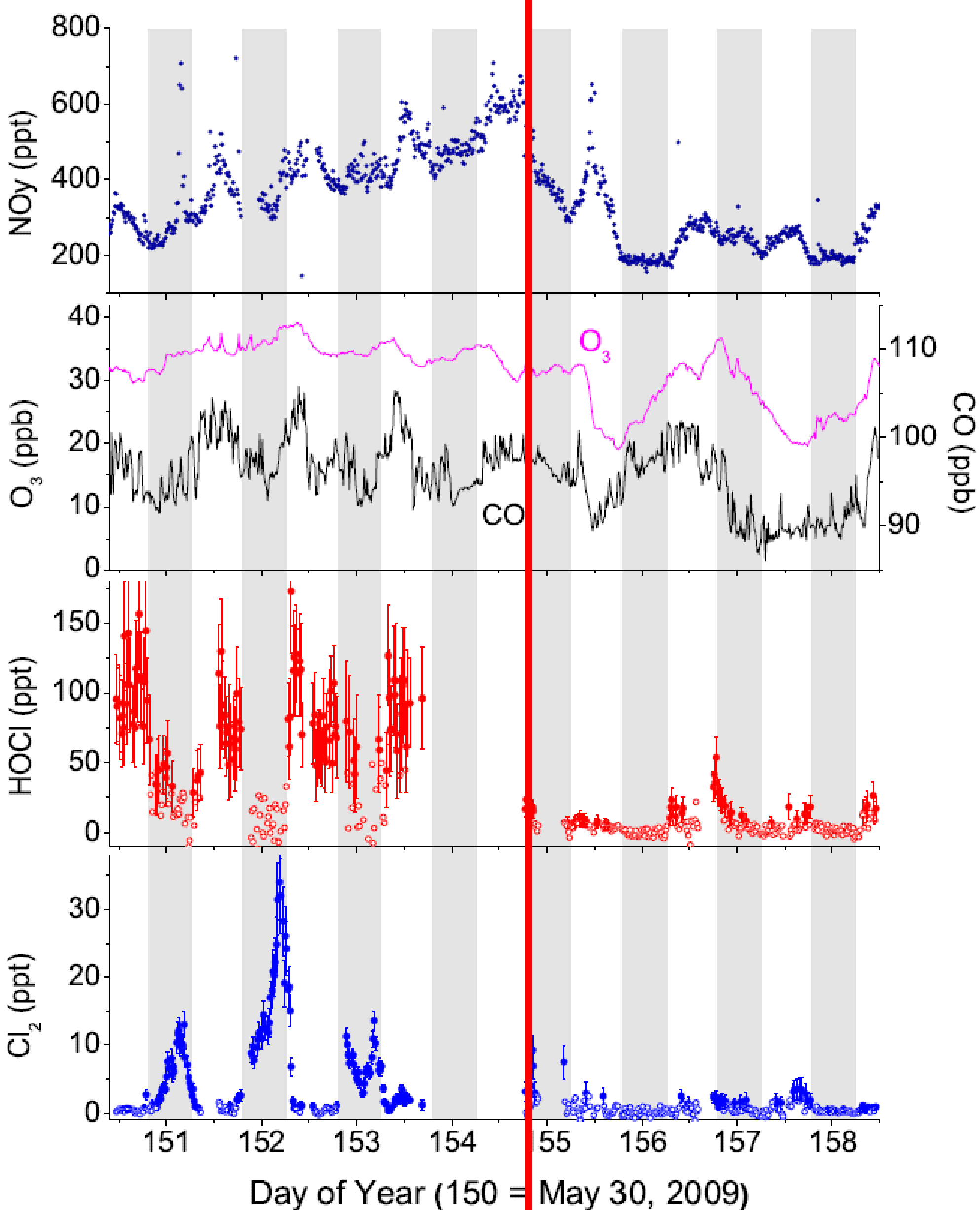
- 1D models roughly reproduce BrO
- 1D models can only reproduce IO with assumption of additional sources
- CIMS data (Lawler et al., 2009, 2011, 2013):
  - Br_2, BrCl
  - HOCl, Cl_2
  - I_2

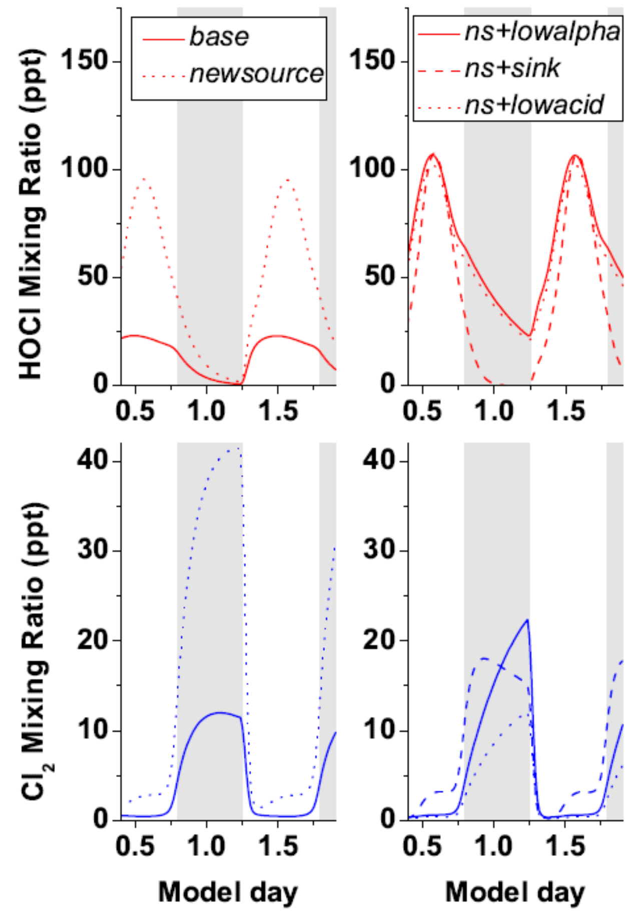
  → much harder to explain with model
- Very large BrO variability
- IO not measured in follow-up study (Pöhler, Frieß et al, unpublished)
- Very little or no BrO at all other locations that don't have obvious additional sources!

Read et al., 2008

Measurements by John Plane's group with LP-DOAS, Nov 2006 - June 2007, large variability

Reactive chlorine

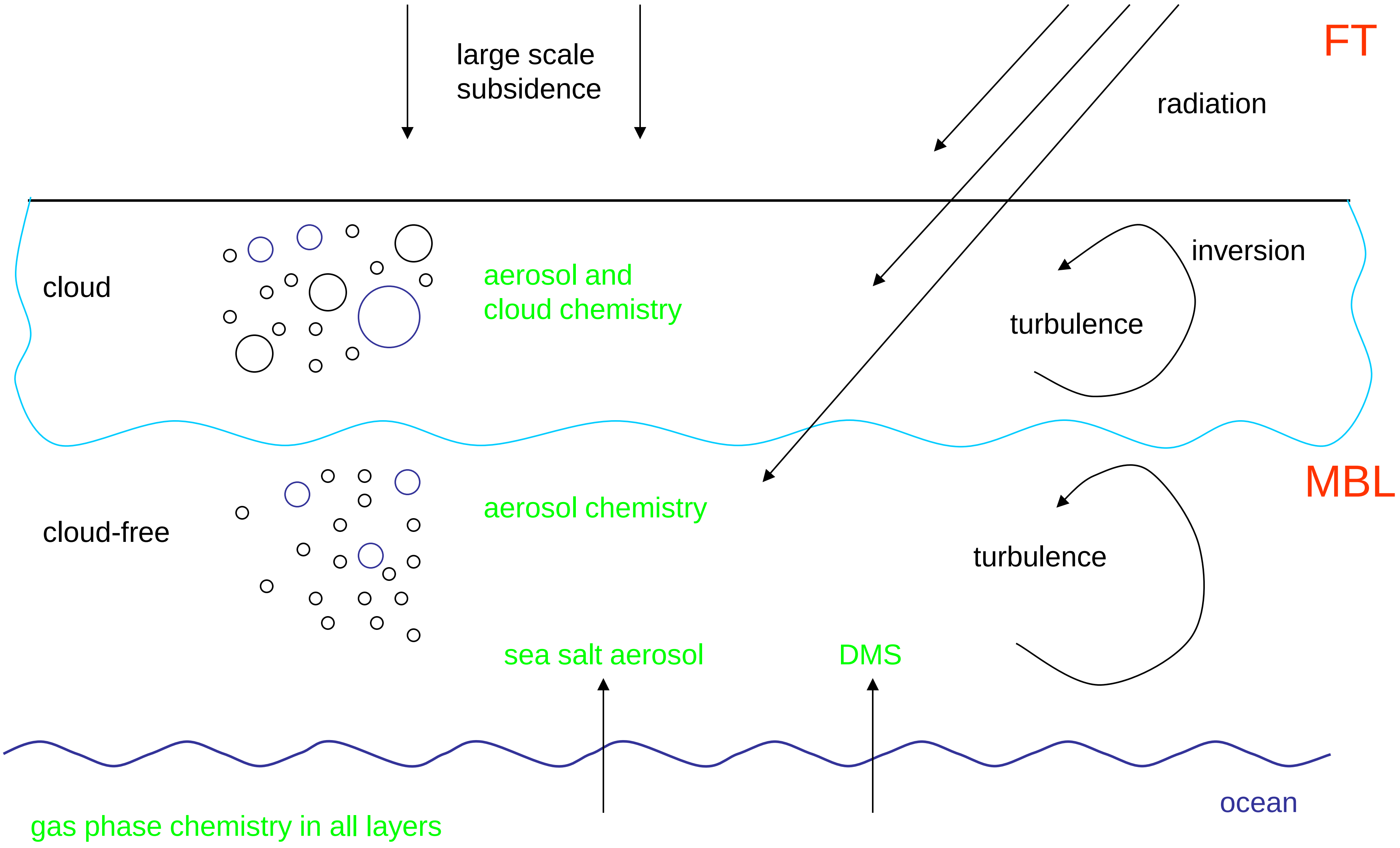




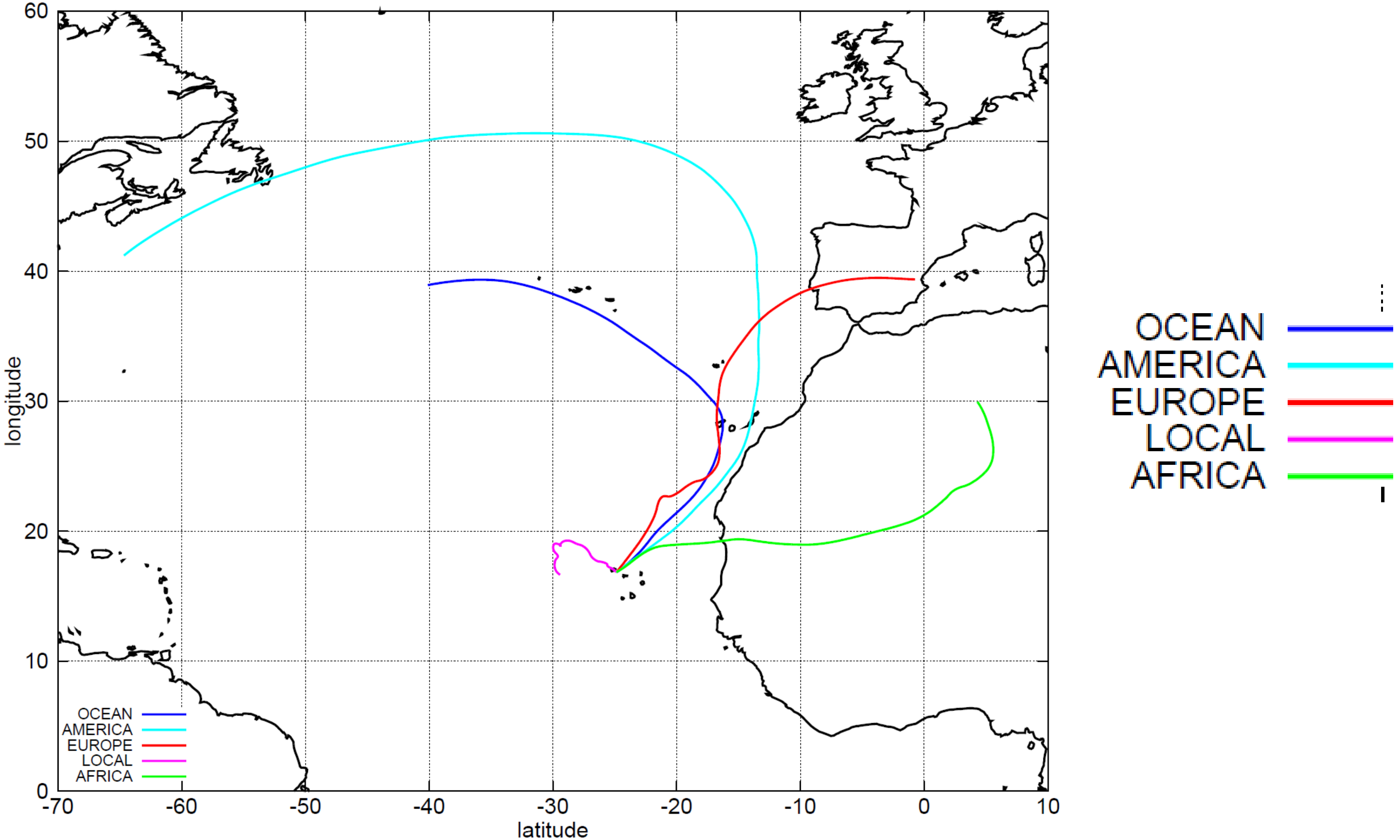
15% of CH_4 oxidation via Cl atoms!

Lawler et al., 2011

MISTRA: One-dimensional MBL model

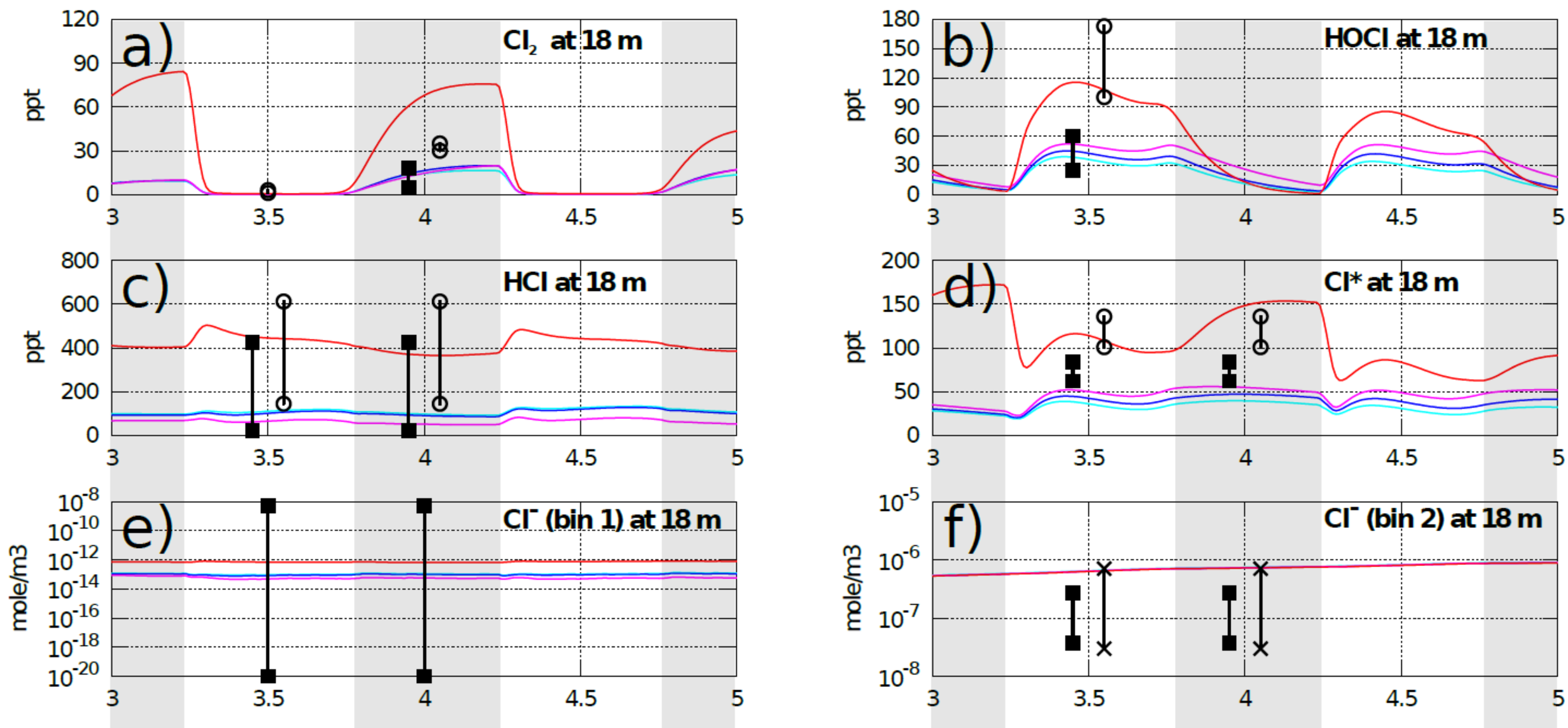


Cape Verde



Sommariva, von Glasow, , Env. Sci. Techn., 2012

Chlorine

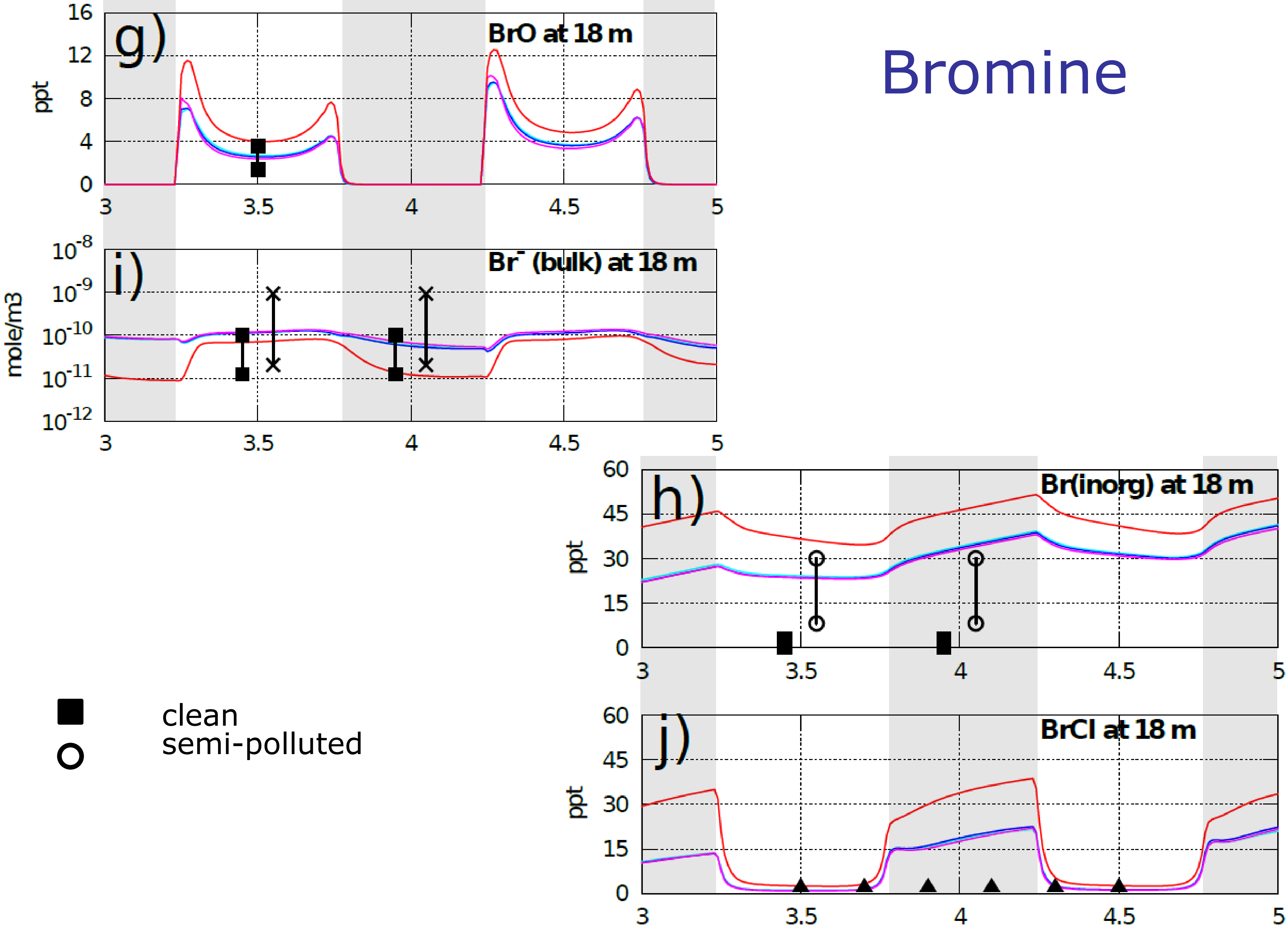


■ clean

○ semi-polluted

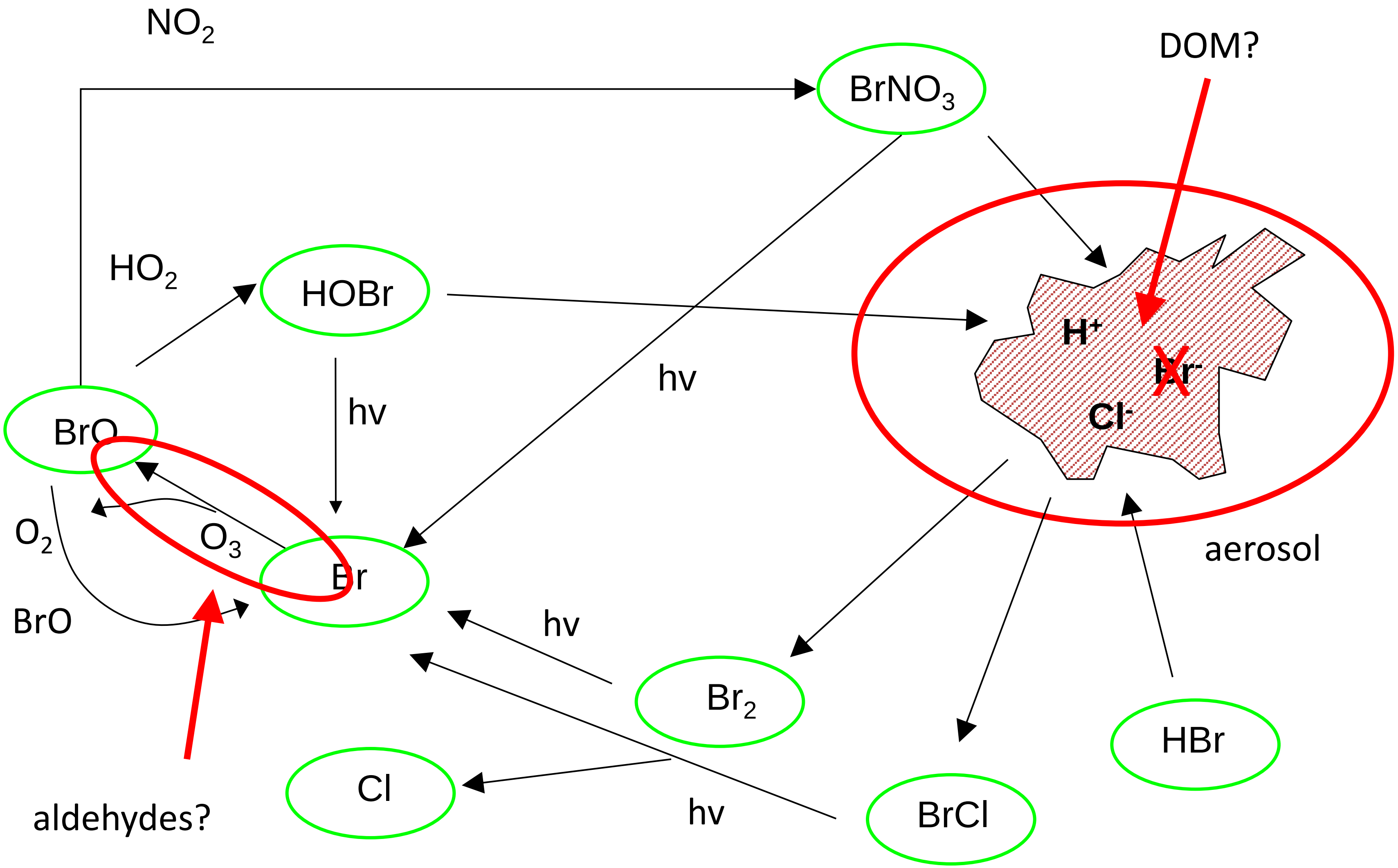
Sommariva, von Glasow, Env. Sci. Techn., 2012

Bromine

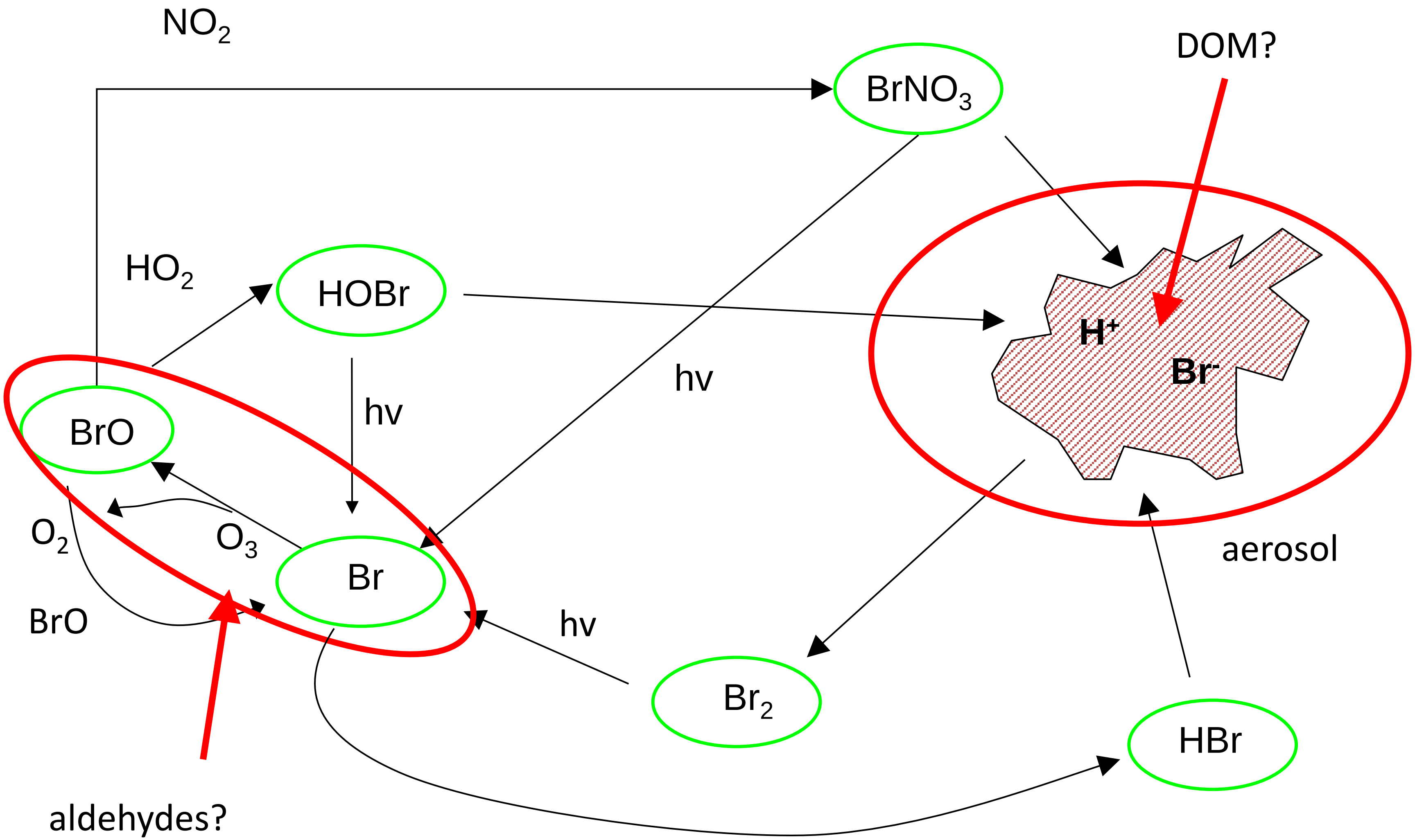


Sommariva, von Glasow, Env. Sci. Techn., 2012

If bromine explosion is too efficient
➔ release of BrCl rather than Br_2



What could make bromine release less efficient?



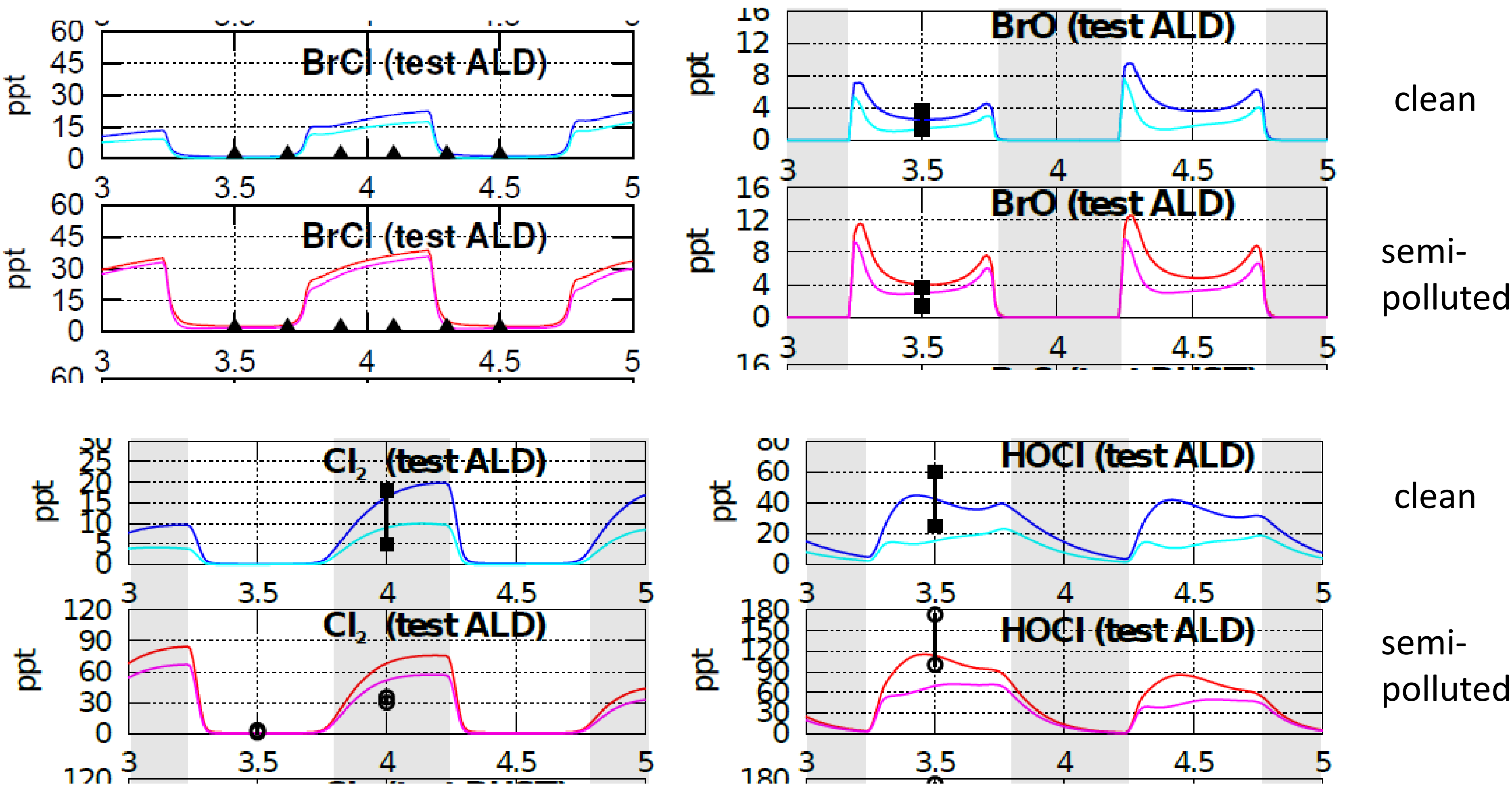
Gas phase "break"

Main reaction: $Br + O_3 \rightarrow BrO + O_2$

Competition: $Br + HCHO \rightarrow .. \rightarrow HBr + CO + HO_2$

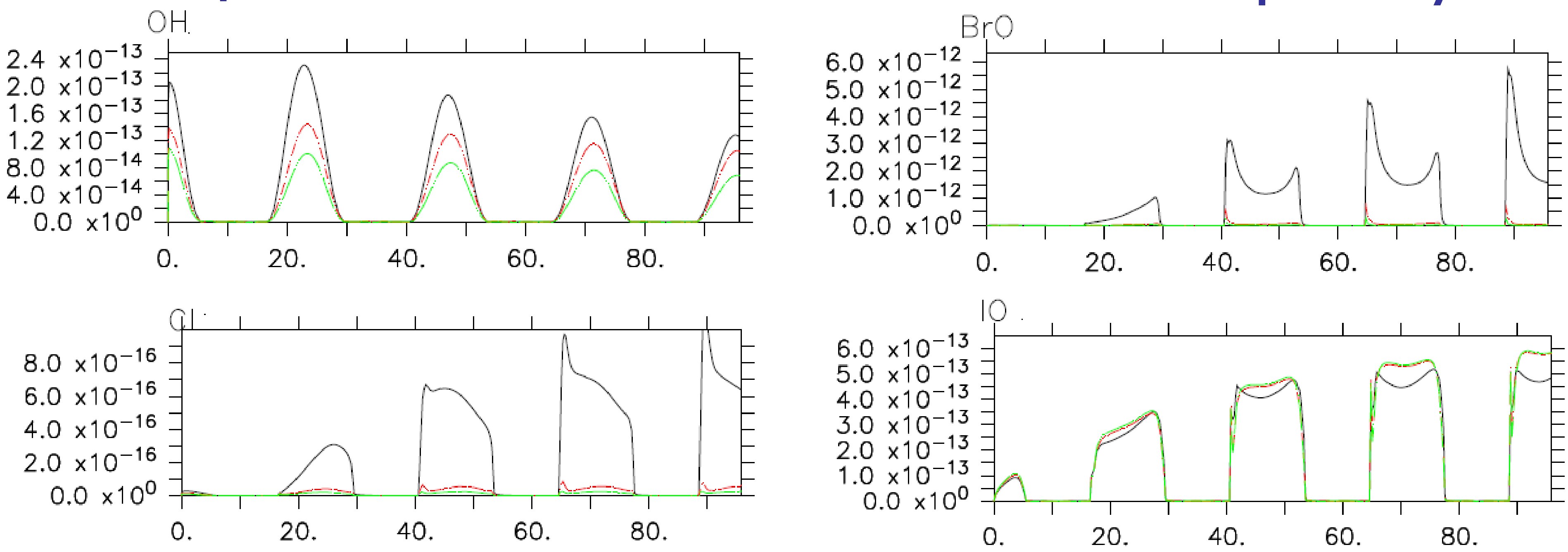
$HCHO$: ~350ppt → 500 ppt
Mahajan et al., 2010

CH_3CHO: ~10 → ~900 ppt
Read et al., 2009



Sommariva, von Glasow, Env. Sci. Techn., 2012

Impact of OVOC on oxidative capacity



base case (similar to Sommariva and von Glasow, 2012)

+0.8 ppb HCHO

+1.8 ppb lumped higher aldehydes (reactivity weighted)

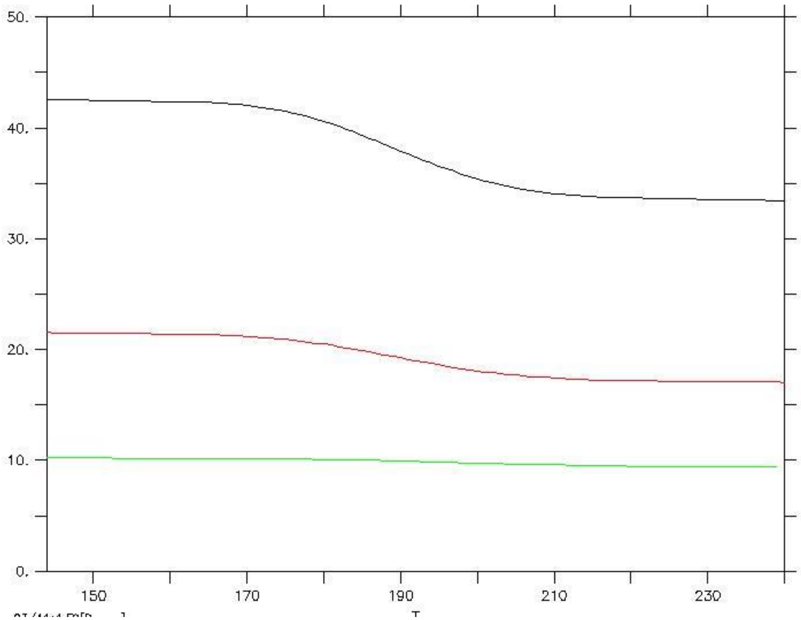
⇒ OVOC are efficient sinks for OH, Cl and Br but not for I

BUT: if aldehydes are main reason for low BrO, Br^- would not be depleted

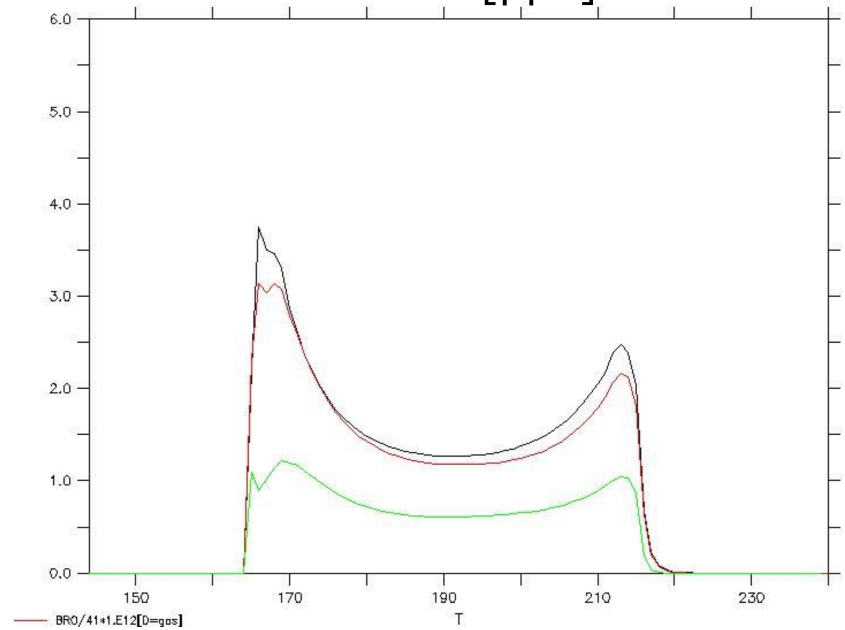
Volkamer, Sommariva, von Glasow, unpublished

Impact of O_3 levels

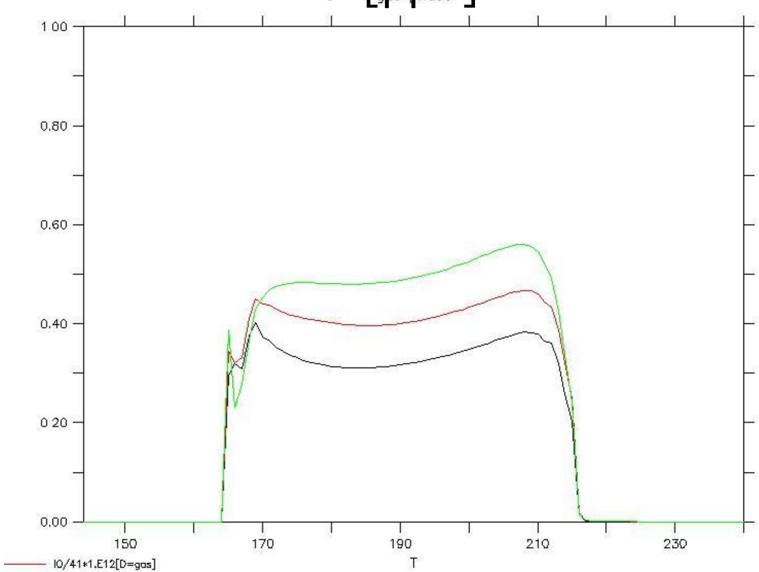
O_3 [ppb]



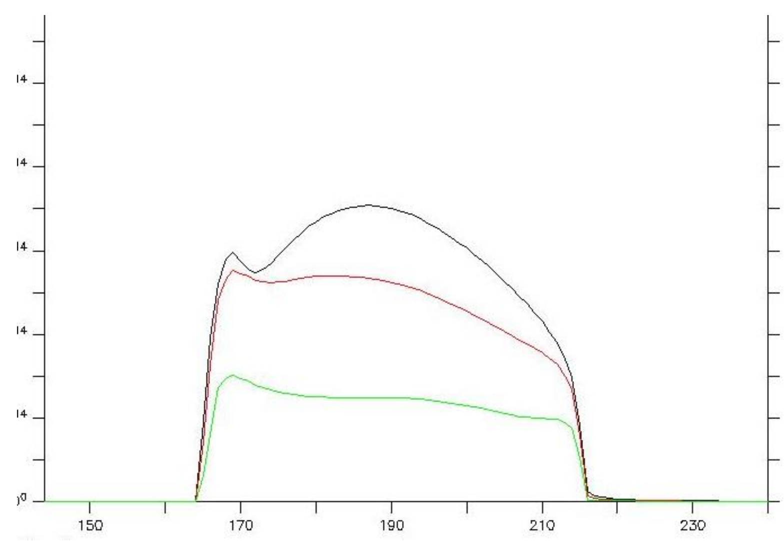
BrO [ppb]



IO [ppb]



Cl



Aqueous phase "break"

Main reaction: $HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$

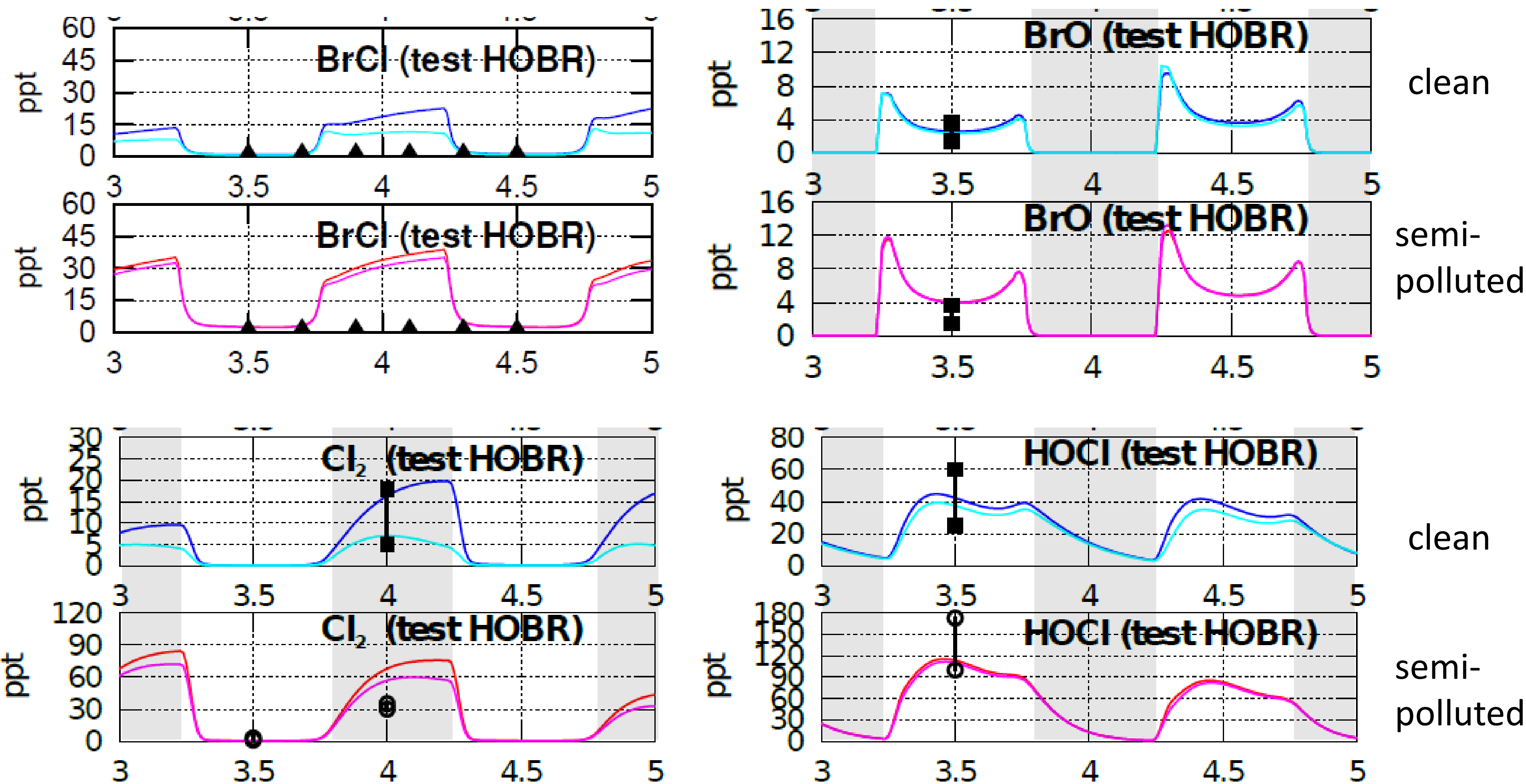
Competition: $HOBr + A \rightarrow Br^-$

A e.g. DOM

Pseudo-1st order:

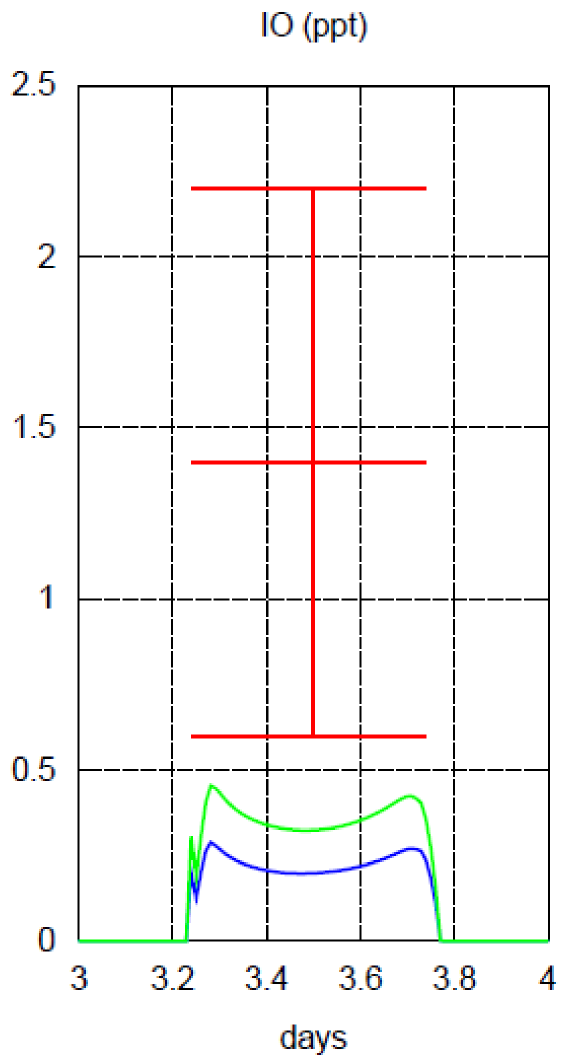
$k_{Cl} = 1\times10^{1}s^{-1}$

$k_{Br} = 1\times10^{4}s^{-1}$



Sommariva, von Glasow, Env. Sci. Techn., 2012

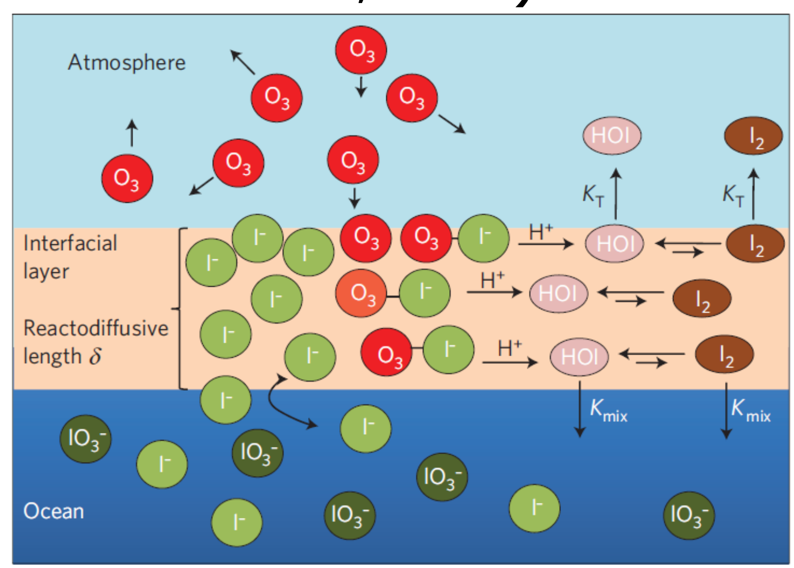
IO: Additional fluxes needed



--- measured
--- mean fluxes
--- max fluxes

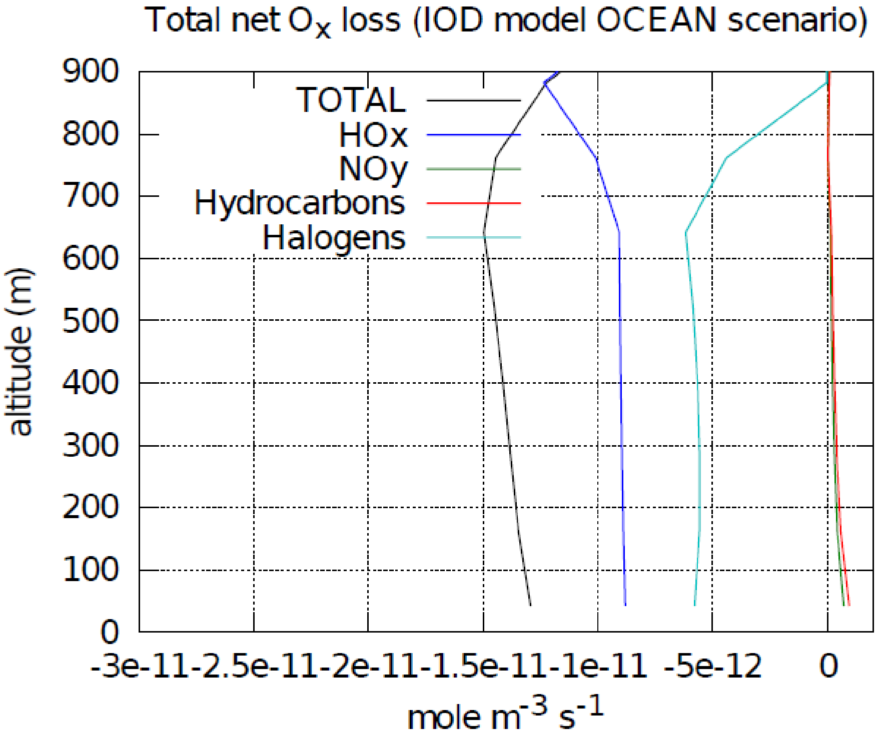
- Graph shows modelled IO using measured precursors (mainly org-I)
  - Not enough
- Additional sources of iodine
  - Most likely explanation: reaction of ozone of ocean surface

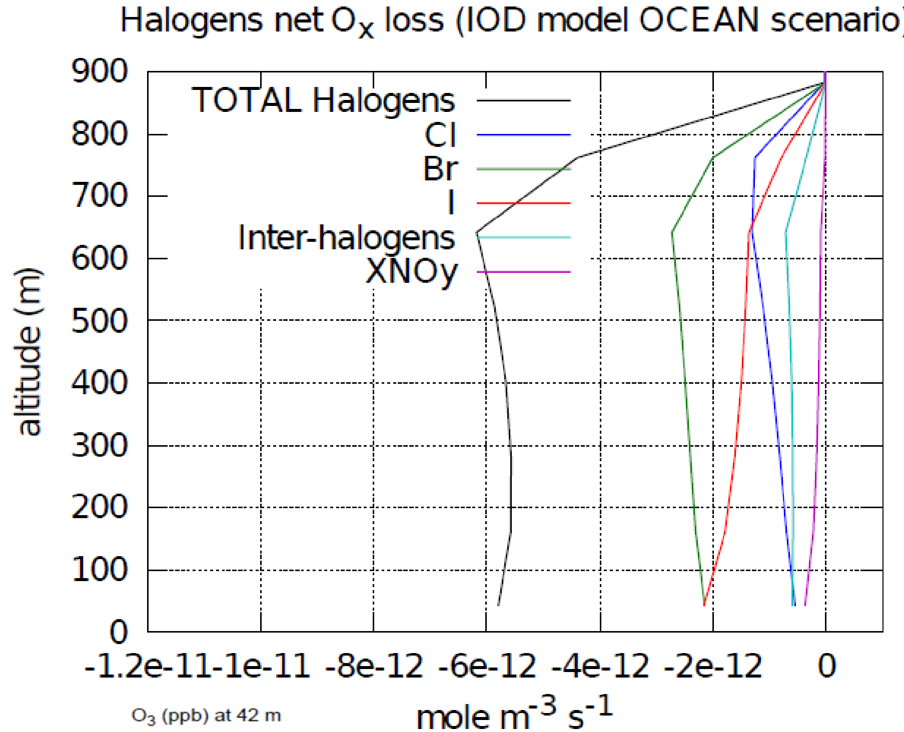
    $O_3 + I^- \rightarrow HOI / I_2$
  - Recent lab studies support this (Carpenter et al., Nat Geosc., 2013)
- I_x mechanism development (Sommariva et al., 2012)

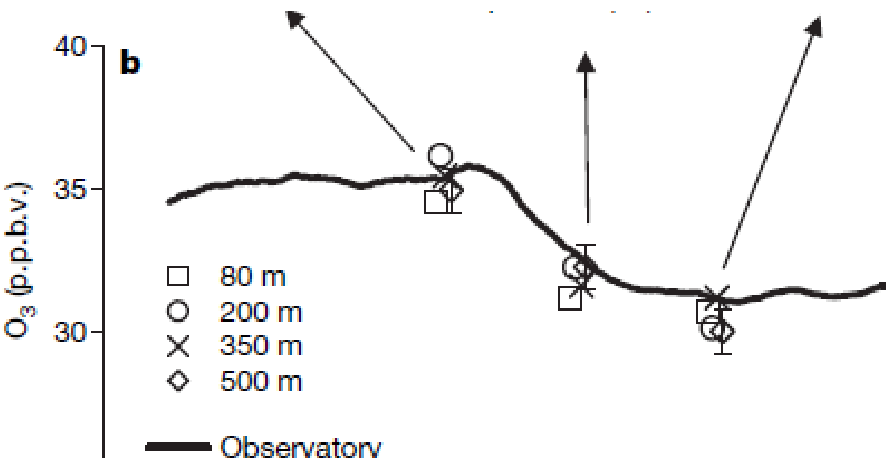


Jones et al., 2010; Mahajan et al., 2010; Sommariva, von Glasow, 2012; Grossmann et al., 2013

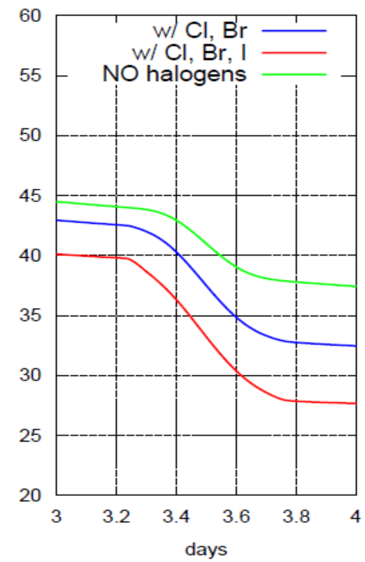
O_3 loss







Read et al., 2008



Br_x, I_x (Cl_x): 35–40% of total chemical ozone destruction

Sommariva, von Glasow, 2012

So, Daddy – what are the key open questions and how do we move this exciting field forward??

Some open questions

- Bromine release from sea salt seems to be too efficient in 1D model (Sommariva and von Glasow, 2012)
- Pathway of release of chlorine from sea salt (other than acid displacement) not fully understood (Lawler et al., 2009, 2011): close link to bromine chemistry
- Sea spray parameterisations still have very large uncertainties, number ~ 2-3x, mass ~ 5x
- Large variability in Br_x (day to day) and I_x (interannually) at Cape Verde – why?
- Causes:
  - Chemistry? Gas phase or aqueous phase?
  - Meteorology? Rain out, source variability, vertical/horizontal mixing?
  - Combination of these? dependent on location and time?
- Field data:
  - Field data base has increased a lot (especially through TIRERO), missing: seasonal/interannual variability and drivers for this, detection limit
  - Instrument intercomparison would be useful
- Recent reviews
  - Saiz-Lopez et al., Chem Rev, 2012: iodine chemistry
  - Saiz-Lopez and von Glasow, Chem. Soc. Rev., 2012: halogens in troposphere

UEA attempts to improve understanding

- NERC TropHal (Leeds, UEA):
  - Focus on mechanism and parameterisation improvement (UEA), global model runs (TOMCAT, Leeds)
- NERC IGAP (UEA):
  - Postdoc starting 01 Sept
  - WRF-Chem, nested, high resolution, driven by RAQMS
  - Goals:
    - Improve UEA halogen scheme in WRF (CBM-Z); add glyoxal
    - Investigate complex photochemistry, multiphase chemistry and role of meteorological factors including convection and cloud effects on transport and chemistry
    - Quantify the impacts on tropospheric oxidation capacity and climate forcing.
    - Close gap between highly detailed box and 1D models and coarse resolution global 3D models
  - Comparison with field data:
    - TORERO/EqPOS data
    - North Atlantic data (mainly Cape Verde)

Thank you!