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Modelling iodine chemistry

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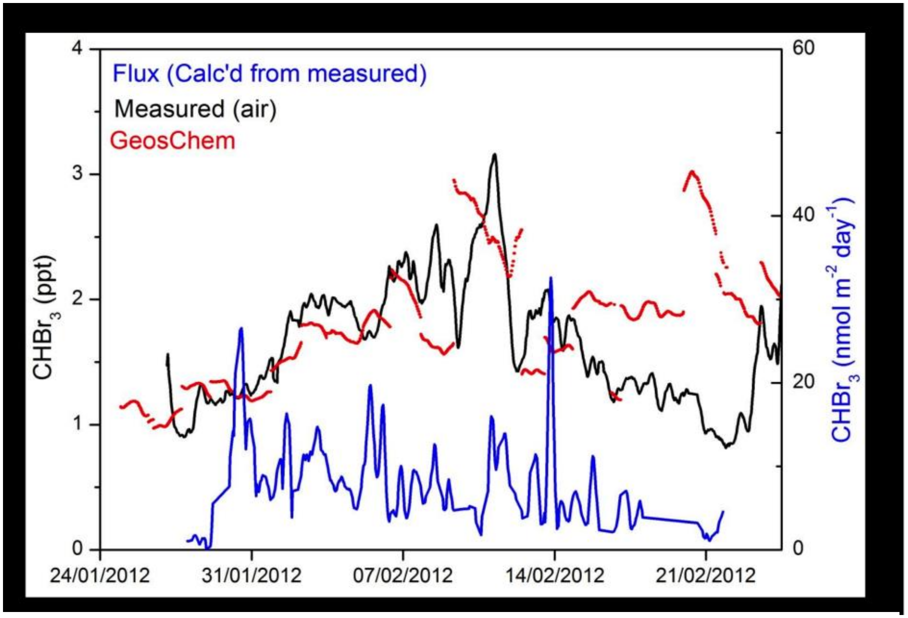
TORERO, CAST + CONTRAST Science teams

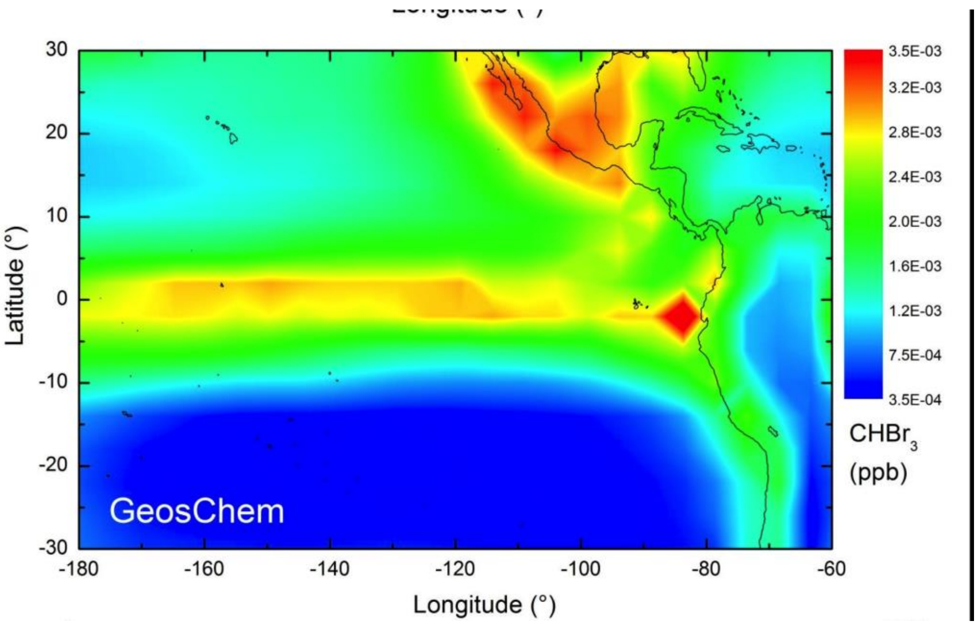
NERC SCIENCE OF THE ENVIRONMENT

National Centre for Atmospheric Science NATURAL ENVIRONMENT RESEARCH COUNCIL

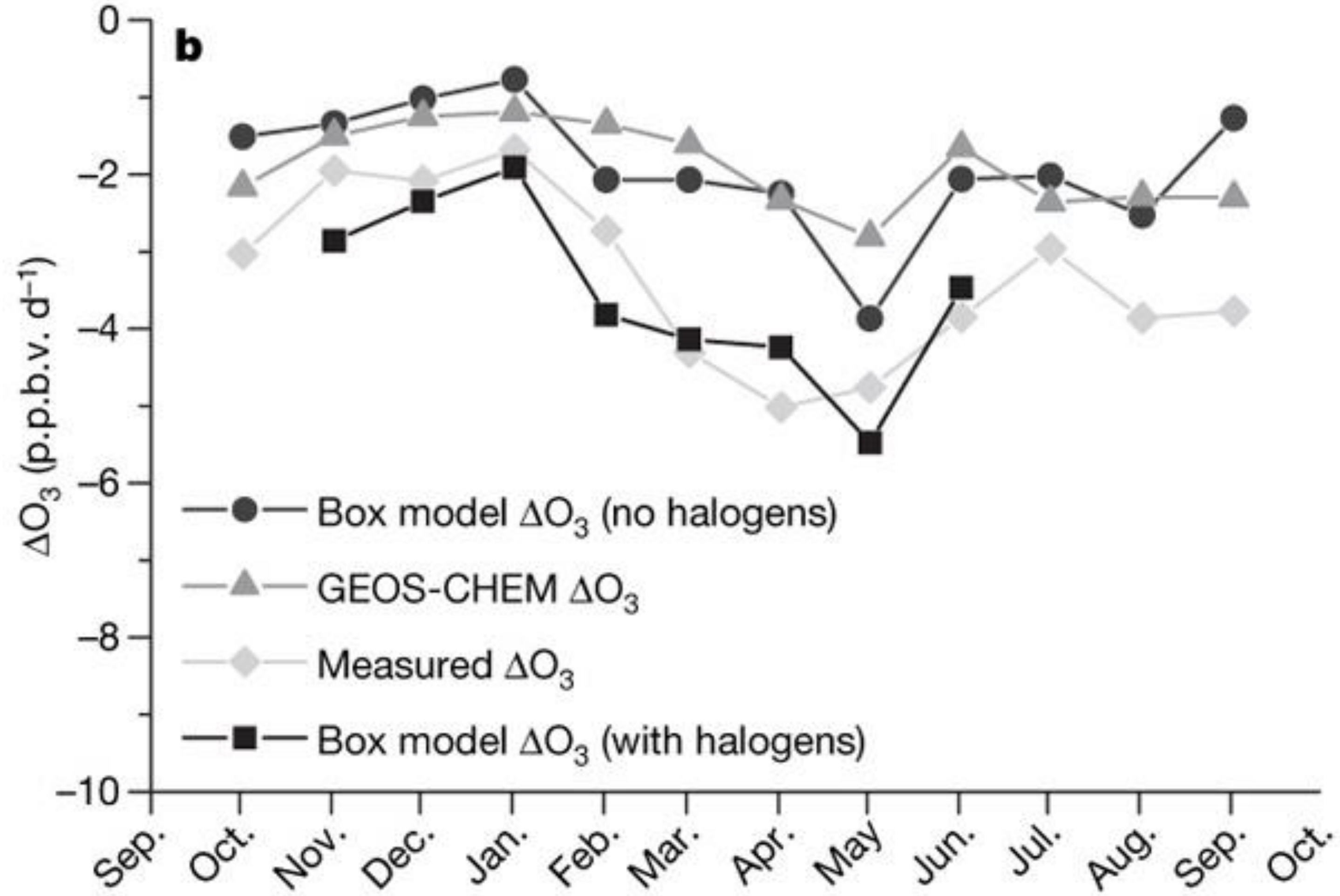
*did all the work, made all the mistakes!

How did we get here?





Historical interest in halogens

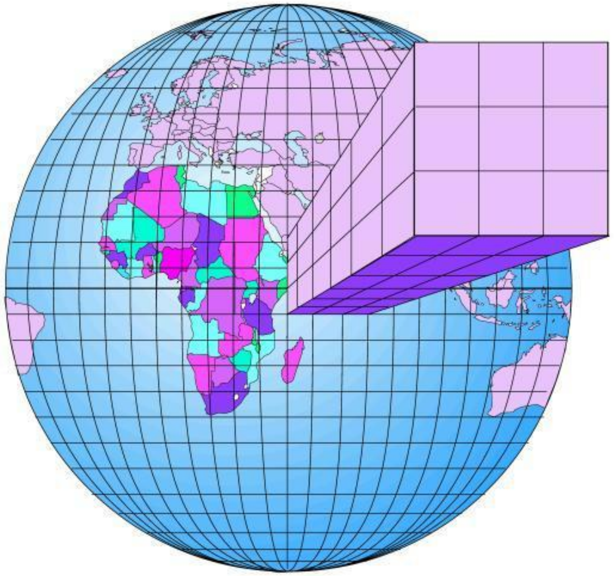


Read et al., 2008

GEOS-Chem

- Bromine chemistry
- Justin Parrella et al., 2012
- **Johan Schmidt**

- Develop an iodine scheme



Emissions

Species	Emissions (Tg I yr^{-1})
CH_3I	0.464
CH_2I_2	0.183
CH_2ICl	0.122
CH_2IBr	0.794
I_2	0.138
HOI	1.429

Emissions

Organics - Jones et al (2010)

Inorganic - Carpenter et al (2013)

Table 2. Gas Phase Iodine reactions, in form: $A \cdot \exp(\frac{(\frac{E}{R})}{T})$

Reaction Reference

- $I_2 \xrightarrow{hv} 2I$
- $HOI \xrightarrow{hv} I + OH$
- $IO \xrightarrow{hv} I + [O_3]$
- $OIO \xrightarrow{hv} I + O_2$
- $INO \xrightarrow{hv} I + NO$
- $IONO \xrightarrow{hv} I + NO_2$
- $IONO_2 \xrightarrow{hv} I + NO_3$
- $I_2O_2 \xrightarrow{hv} 2IO$
- $CH_3IT \xrightarrow{hv} I + (CH_3)$
- $CH_2I_2 \xrightarrow{hv} 2I + (CH_2)$
- $CH_2ICl \xrightarrow{hv} I$
- $CH_2IBr \xrightarrow{hv} I$
- $C_2H5I \xrightarrow{hv} I$
- $C_3H_7I \xrightarrow{hv} I$

Rxn ID	Reaction	Rate	E/R	Citation
M1	$I + O_3 \rightarrow IO + O_2$	2.10E-11	-830	[Atkinson et al, 2007]
M2	$I + HO_2 \rightarrow HI + O_2$	1.50E-11	-1090	[Sander et al, 2011]
M3	$I_2 + OH \rightarrow HOI + I$	2.10E-10	-	[Atkinson et al, 2007]
M4	$HI + OH \rightarrow I + H_2O$	1.60E-11	440	[Atkinson et al, 2007]
M5	$HOI + OH \rightarrow IO + H_2O$	5.00E-12	-	[Riffault et al, 2005]
M6	$IO + HO_2 \rightarrow HOI + O_2$	1.40E-11	540	[Atkinson et al, 2007]
M7	$IO + NO \rightarrow I + NO_2$	7.15E-12	300	[Atkinson et al, 2007]
M8	$HO + CH_3\ IT \rightarrow H_2O + I\ (CH_2I])$	4.30E-12	-1120	[Atkinson et al, 2008]
M9	$INO + INO \rightarrow I_2 + 2NO$	8.40E-11	-2620	[Atkinson et al, 2007]
M10	$IONO + IONO \rightarrow I_2 + 2NO_2$	4.70E-13	-1670	[Atkinson et al, 2007]
M11	$I_2 + NO_3 \rightarrow I + IONO_2$	1.50E-12	-	[Atkinson et al, 2007]
M12	$IONO_2 + I \rightarrow I_2 + NO_3$	9.10E-11	-146	[Kaltsoyannis and Plane, 2008]
M13	$I + BrO \rightarrow IO + Br$	1.20E-11	-	[Sander et al, 2011]
M14	$IO + Br \rightarrow I + BrO$	2.70E-11	-	[Bedjanian et al, 1997]
M15	$IO + BrO \rightarrow Br + I + O_2$	3.00E-12	510	[Atkinson et al, 2007]
M16	$IO + BrO \rightarrow Br + OIO$	1.20E-11	510	[Atkinson et al, 2007]
M17	$OIO + OIO \rightarrow I_2O_4$	1.50E-10	-	[Gomez-Martin et al, 2007]
M18	$OIO + NO \rightarrow NO_2 + IO$	1.10E-12	542	[Atkinson et al, 2007]

Table 3. Termolecular Iodine Reactions, in form: $A \cdot \exp(\frac{(\frac{E}{R})}{T}) \cdot (\frac{300}{T})^x$

Rxn ID	Reaction	rate (K_0)	E/R	Exponent (x)	K(∞)	E/R	Fc	Citation
T1	$IO + IO \xrightarrow{O_2} I + OIO$	2.16E-11	180	-	-	-	-	[Atkinson et al, 2007]
T2	$IO + IO \xrightarrow{O_2} I_2O_2$	3.24E-11	180	-	-	-	-	[Atkinson et al, 2007]
T3	$I + NO \xleftrightarrow{M} INO$	1.80E-32	300	-	1.70E-11	9200	0.6	[Atkinson et al, 2007]
T4	$INO \rightarrow I + NO$	2.00E-06	-	1	-	-	-	[Atkinson et al, 2007]
T5	$I + NO_2 \xleftrightarrow{M} IONO$	3.00E-31	300	-	6.60E-11	96000	0.63	[Atkinson et al, 2007]
T6	$IONO \rightarrow I + NO_2$	3.72E-07	-	1	-	-	-	[Atkinson et al, 2007]
T7	$IO + NO_2 \rightarrow IONO_2$	7.70E-31	-	5	1.60E-11	-	0.4	[Atkinson et al, 2007]
T8	$IONO_2 \xrightarrow{M} IO + NO_2$	2.10E+15	-13670	-	-	-	0.6	[Kaltsoyannis and Plane, 2008]
T9	$IO + OIO \xrightarrow{M} loss\ [I_2O_3]$	1.50E-10	-	-	-	-	-	[Gomez-Martin et al, 2007]
T10	$I_2O_2 \xrightarrow{M} IO + IO$	4.00E+12	-9770	-	-	-	0.6	[Kaltsoyannis and Plane, 2008]
T11	$I_2O_2 \xrightarrow{M} OIO + I$	2.50E+14	-9770	-	-	-	0.6	[Kaltsoyannis and Plane, 2008]
T13	$I_2O_4 \xrightarrow{M} 2OIO$	3.80E-02	-	-	-	-	-	[Kaltsoyannis and Plane, 2008]

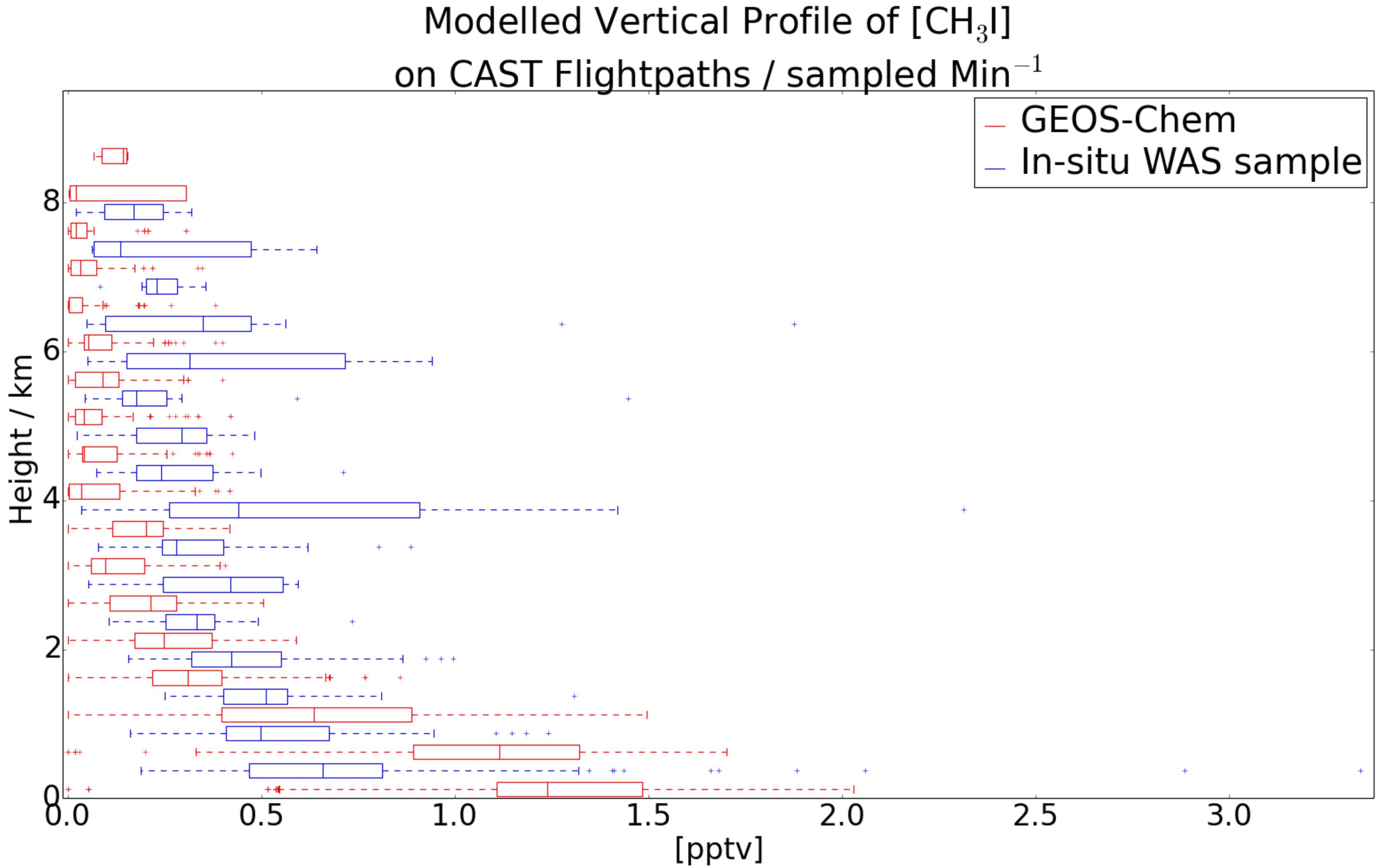
Table 6. Heterogeneous Reactions added

ID	Reaction	uptake coefficient (γ)	Reference
K1	$HI \xrightarrow{\gamma} 0.5I_2$	0.20	[Crowley et al. 2010]
K2	$IONO_2 \xrightarrow{\gamma} 0.5I_2$	0.02	-
K3	$HOI \xrightarrow{\gamma} 0.5I_2$	0.06	-
K4	$IONO \xrightarrow{\gamma} 0.5I_2$	0.02	-
K5	$I_2O_2 \xrightarrow{\gamma}$ aerosol loss	0.01	-
K6	$I_2O_4 \xrightarrow{\gamma}$ aerosol loss	0.01	-

Model assessment

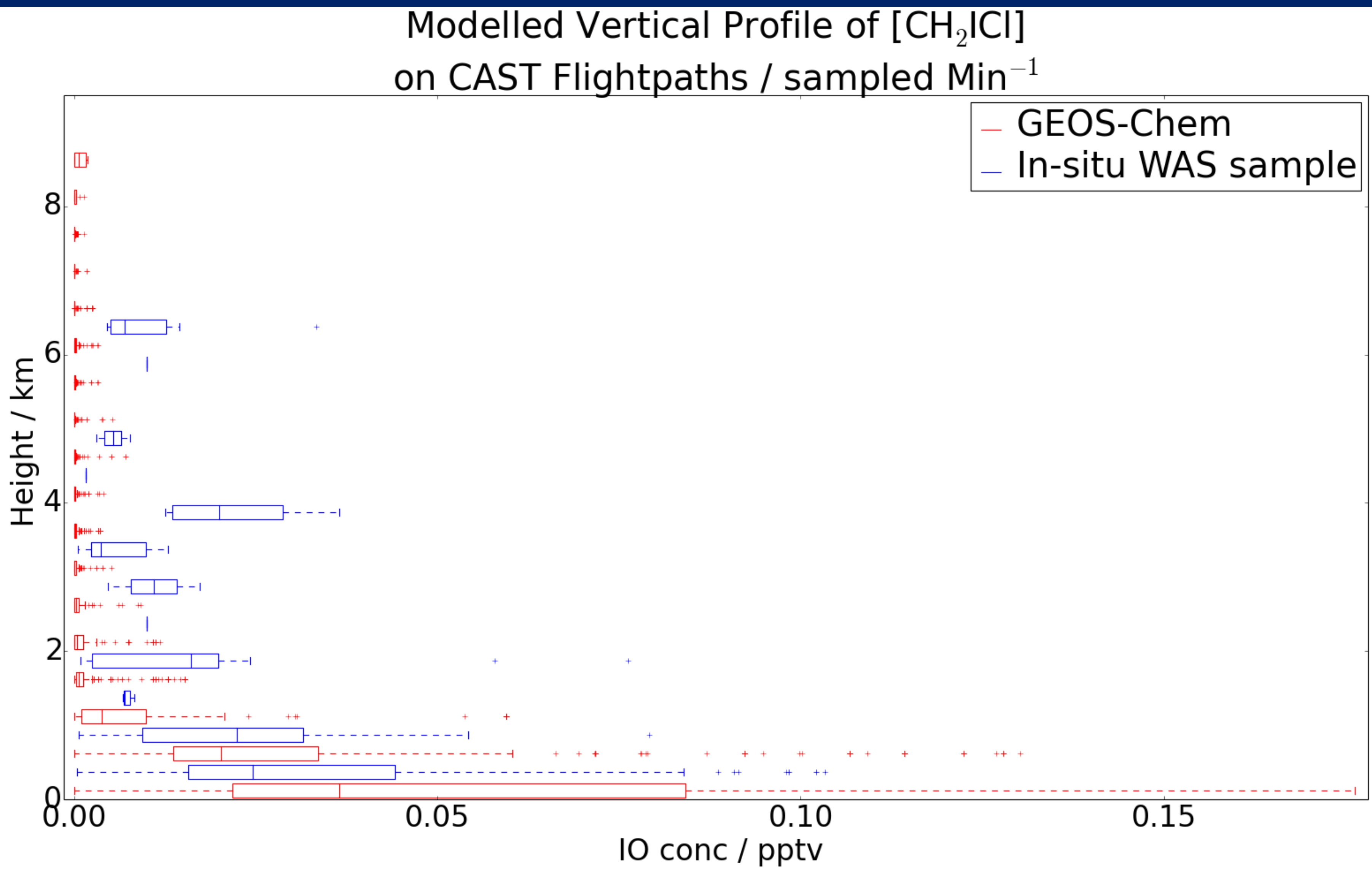
- Compare to available observations
- Halocarbons
- IO observations
- Recent campaigns
  - TORERO
  - CAST / CONTRAST
- Other observations ozone, NOx, etc

CH_3I CAST

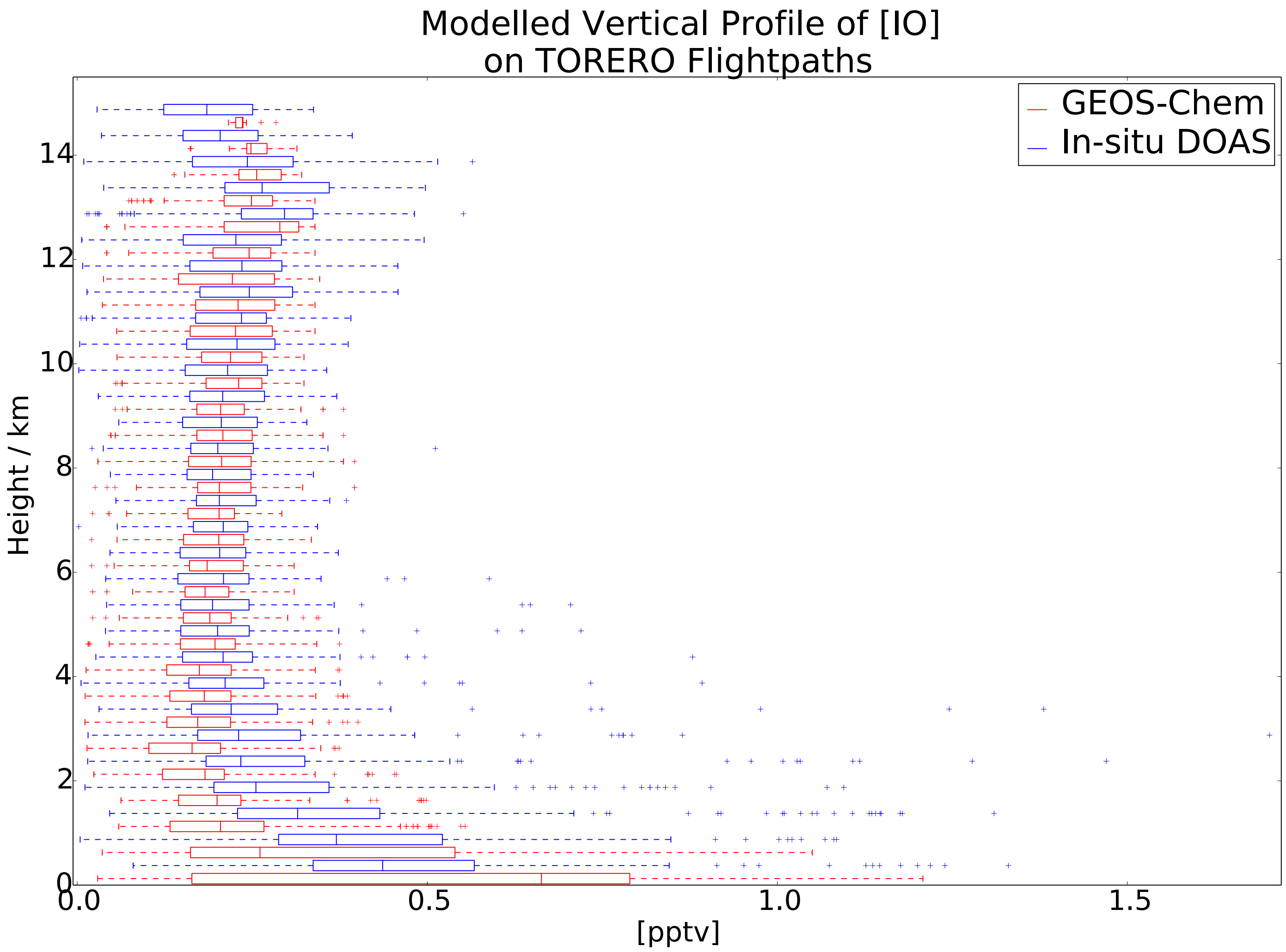


Modelled Vertical Profile of [CH_3I]
on CAST Flightpaths / sampled Min^{-1}
GEOS-Chem
In-situ WAS sample
Height / km
0
2
4
6
8
0.0
0.5
1.0
1.5
2.0
2.5
3.0
[pptv]

CH_2ICl CAST

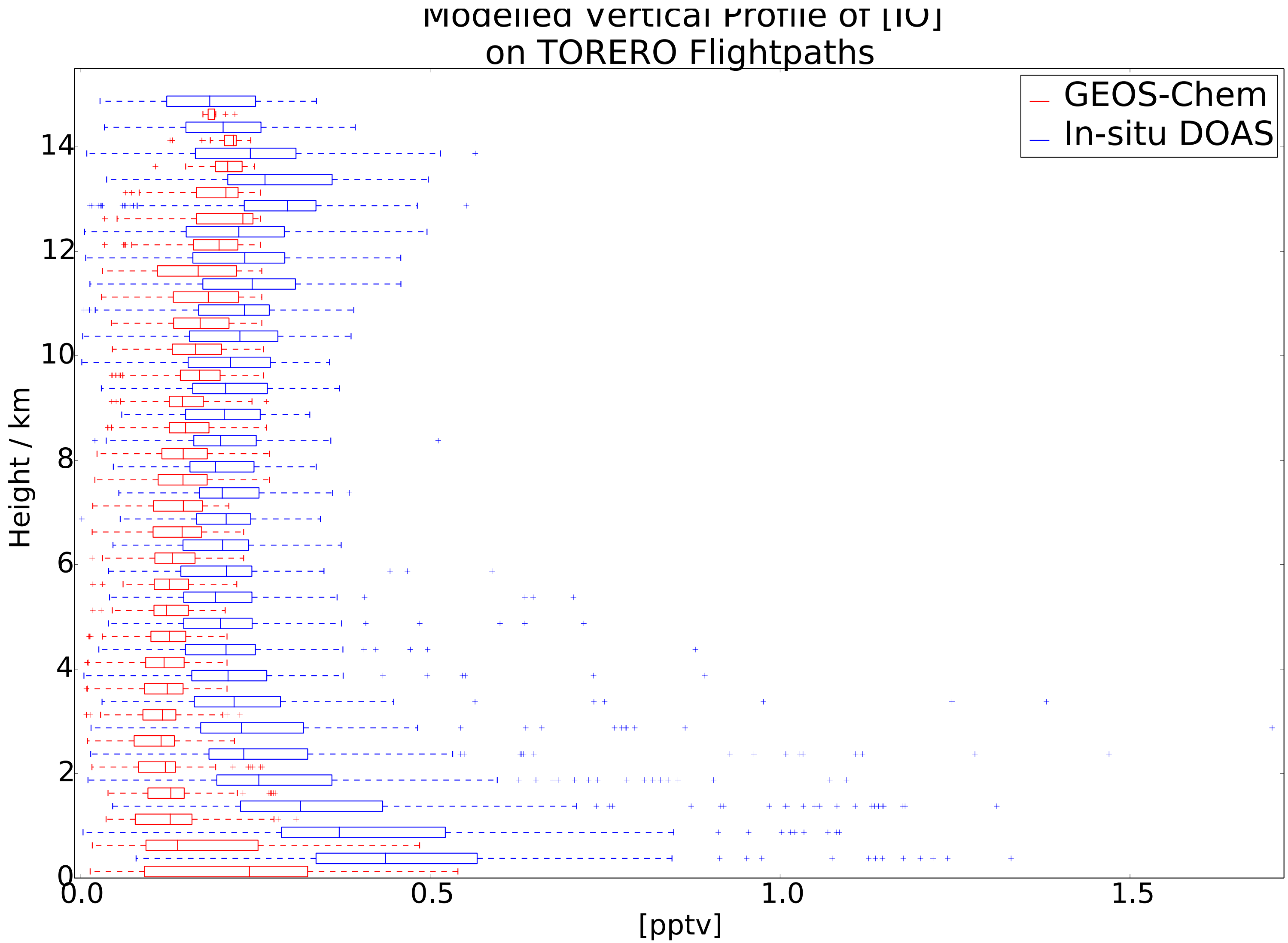

Modelled Vertical Profile of [CH_2ICl]
on CAST Flightpaths / sampled Min^{-1}
GEOS-Chem
In-situ WAS sample
Height / km
IO conc / pptv
0
2
4
6
8
0.00
0.05
0.10
0.15

IO TORERO

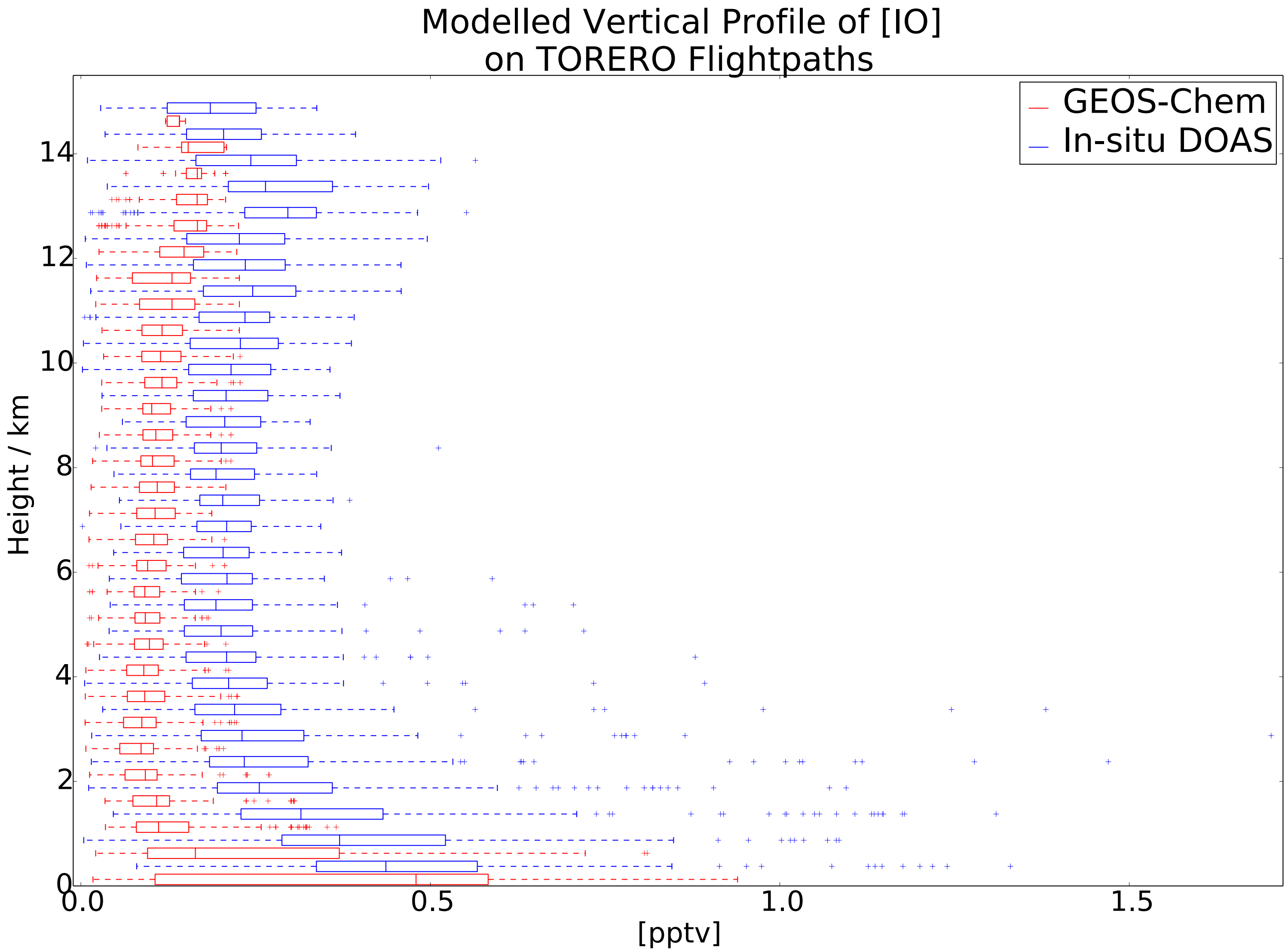


Modelled Vertical Profile of [IO]
on TORERO Flightpaths
GEOS-Chem
In-situ DOAS
Height / km
0
2
4
6
8
10
12
14
0.0
0.5
1.0
1.5
[pptv]

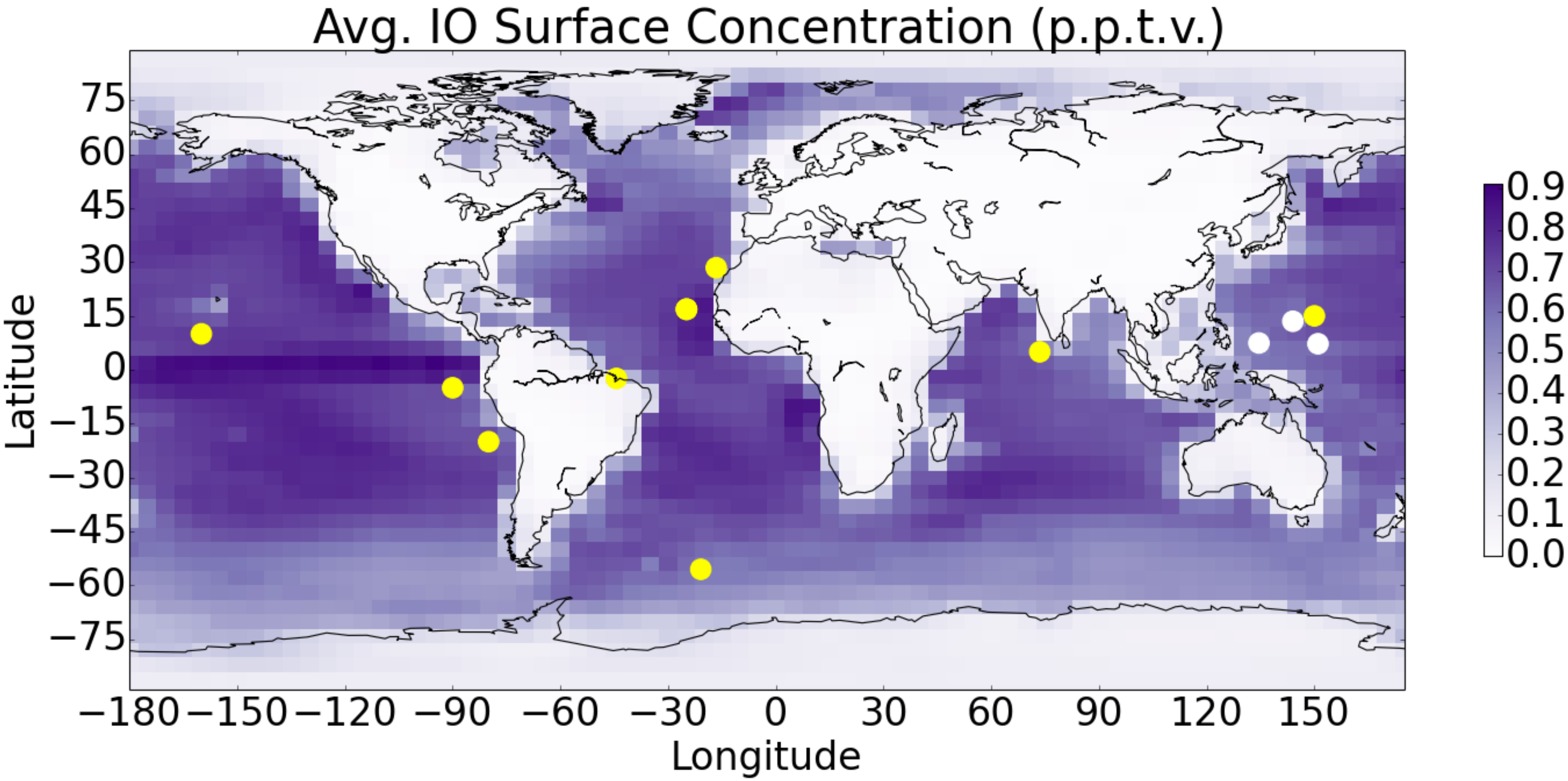
No inorganic source



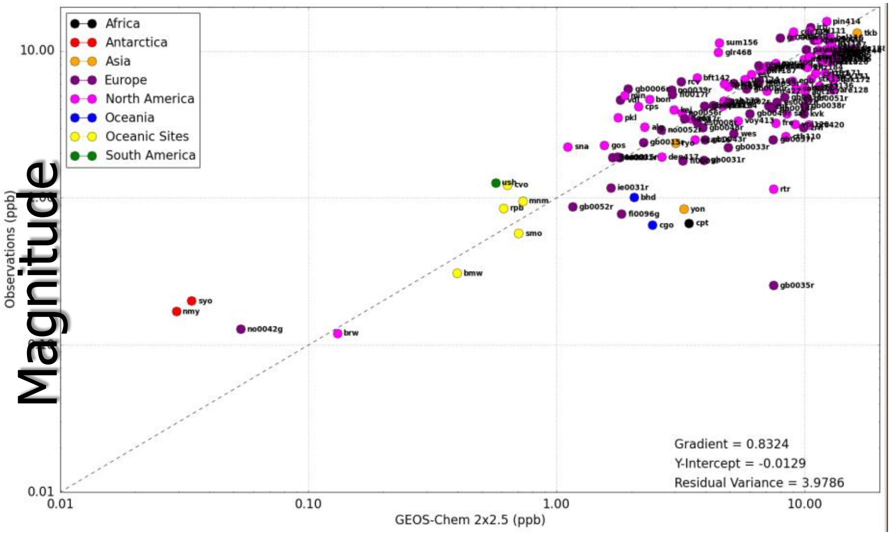
No organic source



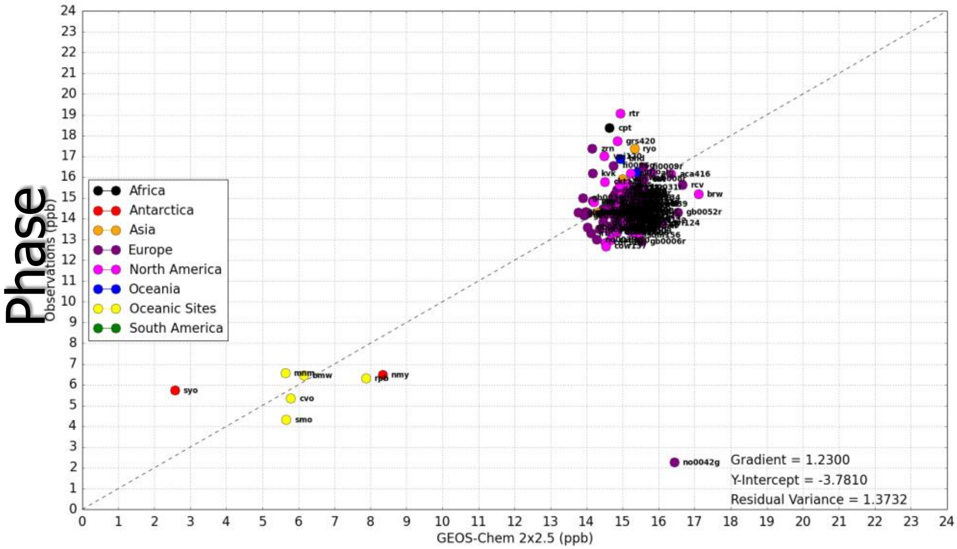
Other observations



Fourier analysis of large ozone dataset



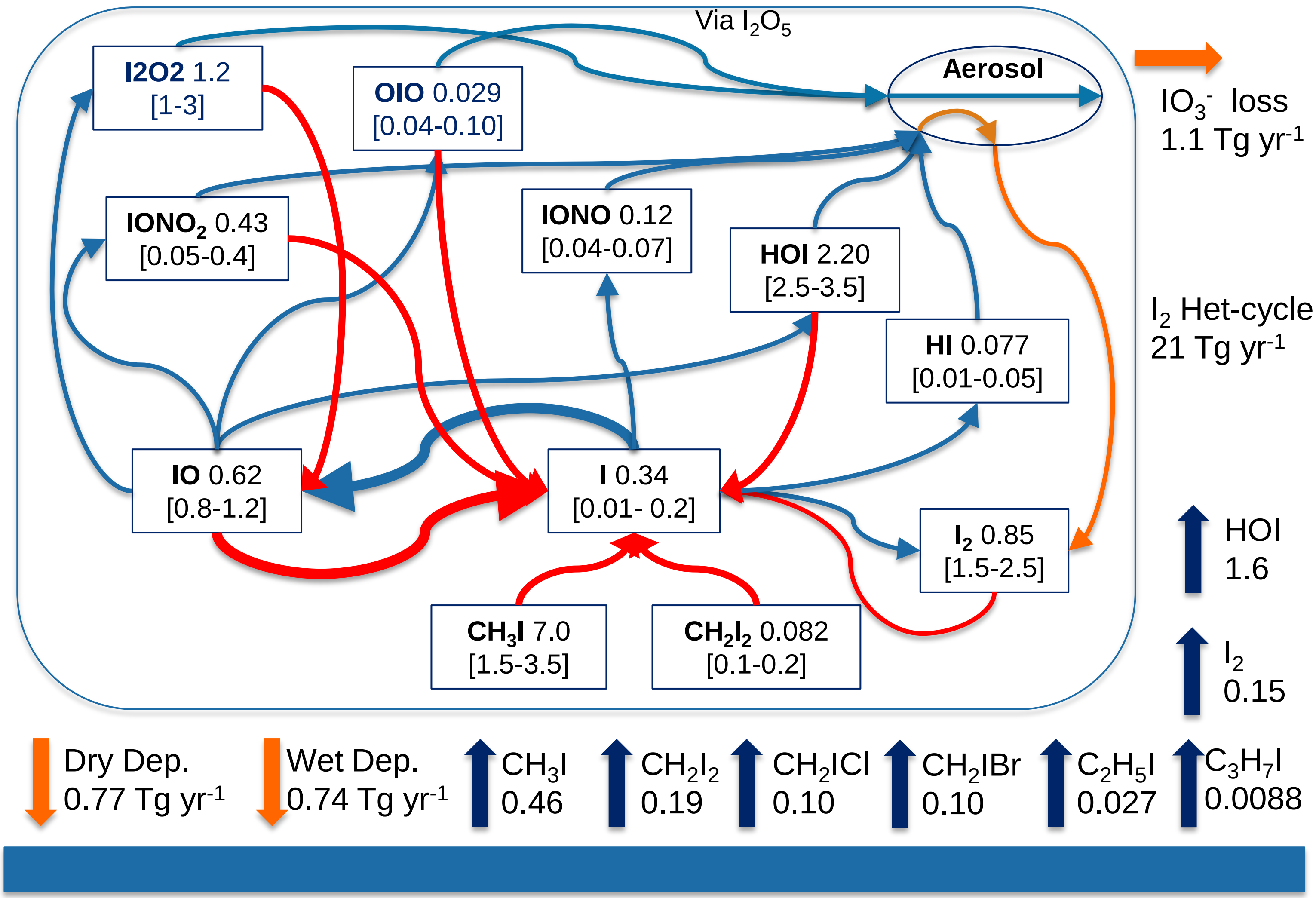
Magnitude



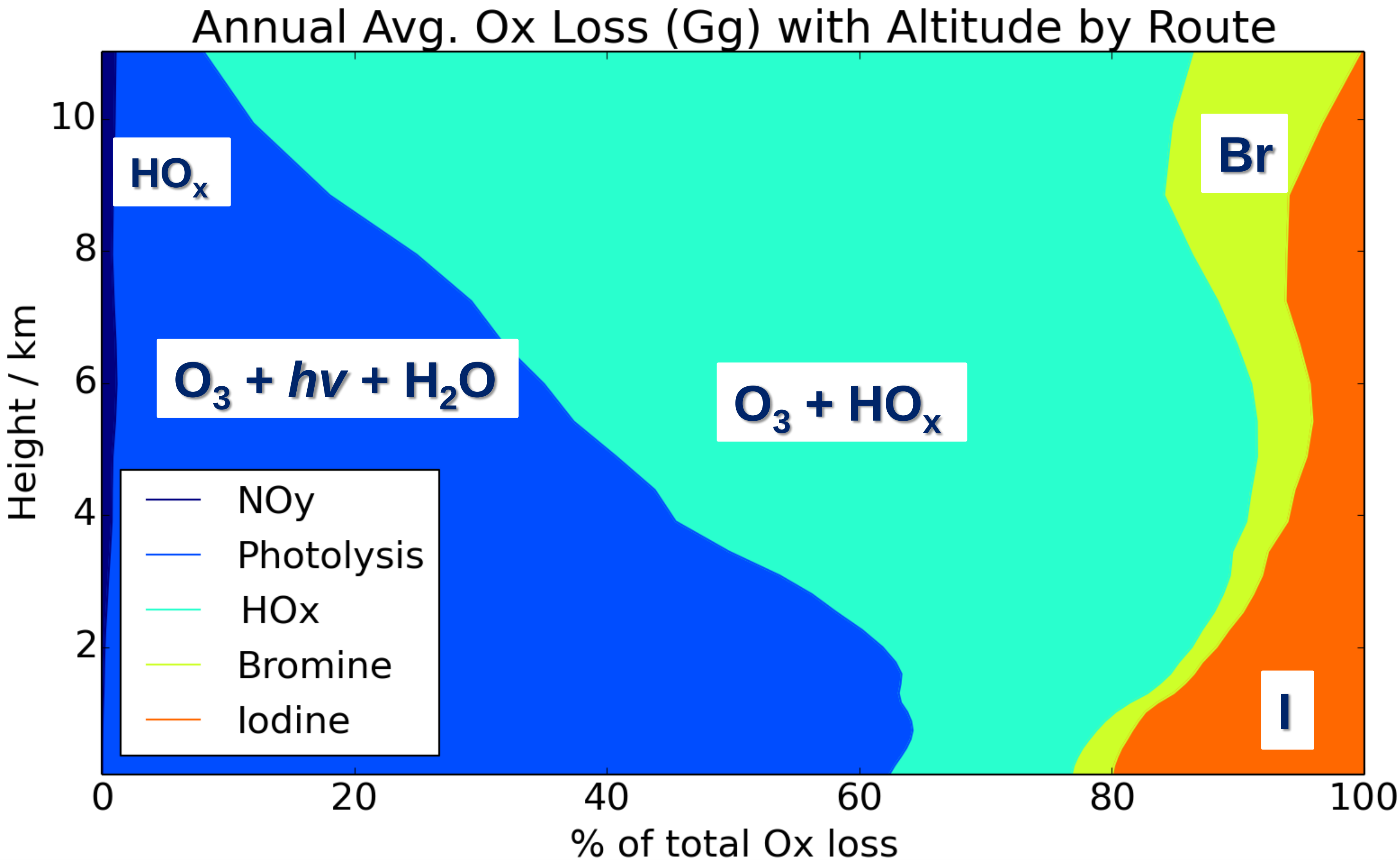
Phase

Iodine Budget

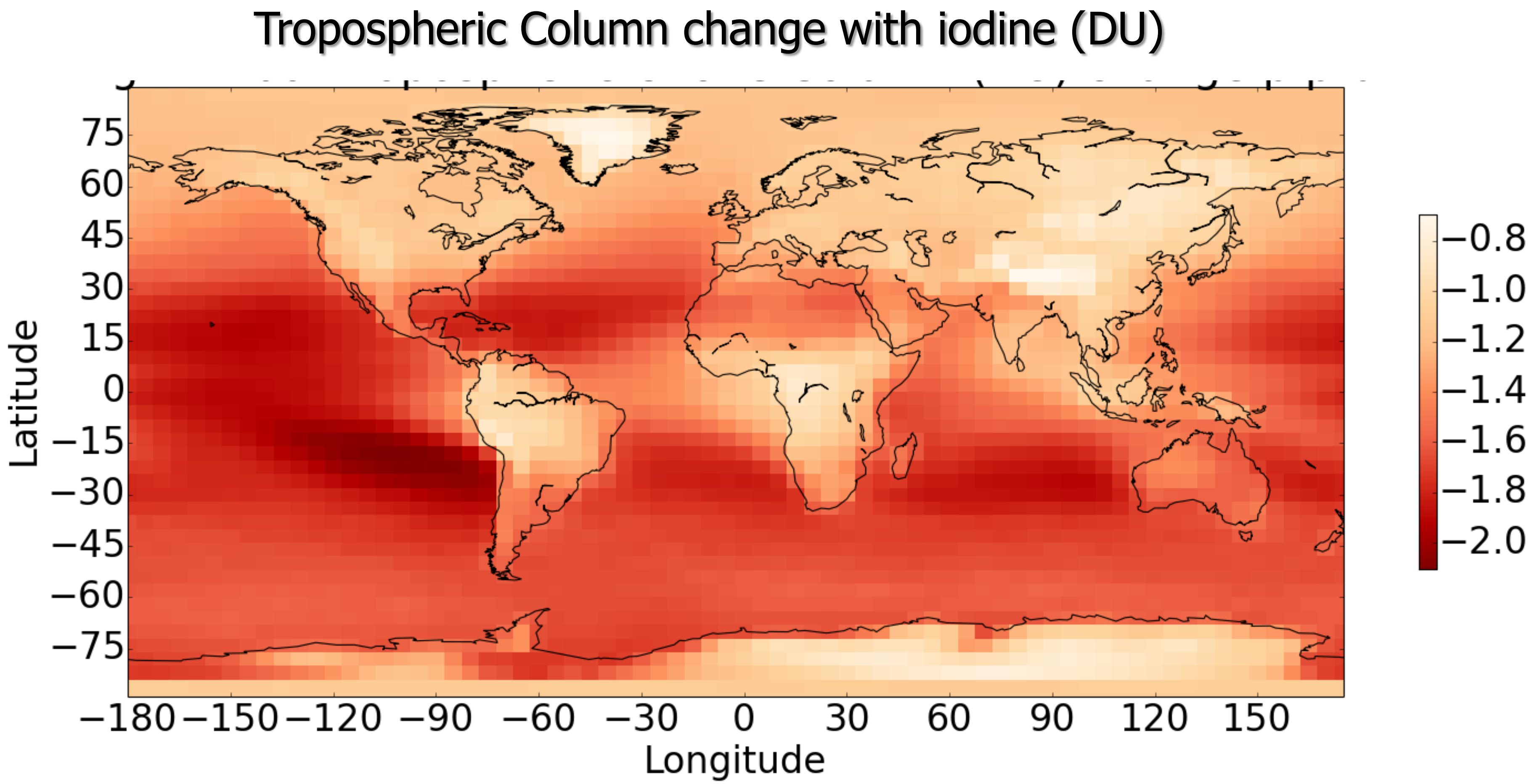
Approx. peak diurnal values at Cape Verde (CV) in pptv in square brackets; mean global burdens (Gg I) RH of species. Red lines = photolysis, blue = chemical pathways, green lines = emission source, orange lines = heterogeneous pathway. Equates to total sources of 2.67Tg, and sinks of 2.26



Ox loss by route



Impacts


Tropospheric Column change with iodine (DU)
75
60
45
30
15
0
−15
−30
−45
−60
−75
Latitude
−180 −150 −120 −90 −60 −30 0 30 60 90 120 150
Longitude
−0.8
−1.0
−1.2
−1.4
−1.6
−1.8
−2.0

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Future work

- Model assessment
  - CAST + CONTRAST, TORERO
  - Other datasets
- Model sensitivity
  - Emissions
  - Kinetics
- Impacts AQ, RF, Health