The role of halogens in the regulation of the oxidative capacity of the Earth's troposphere in low-polluted environments

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Outline

I- Importance of halogen-related processes in the troposphere

Tropospheric halogens processes are important on a global level (Saiz-Lopez et al., 2012b ; Simpson et al., 2015).

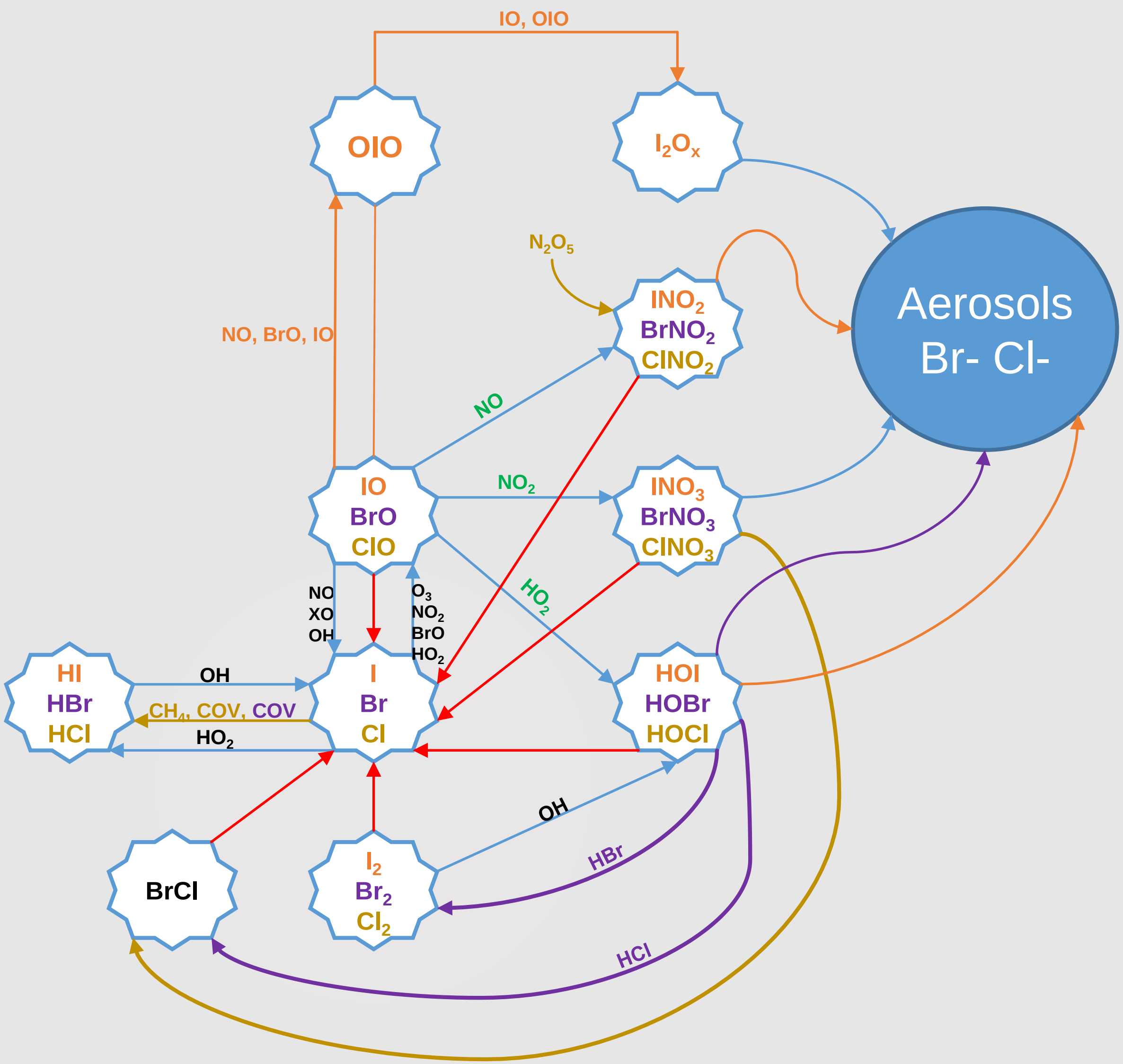
- Halogens consume O_3 and reduce OH primary production, thus change the oxidative capacity of the troposphere
- Halogens oxidize Hg, VOCs, methane and produce SOA

To this day few General Circulation Models (GCMs) have integrated this chemistry.

➡ This work aims to implement the tropospheric halogen chemistry to the GCM LMDz-INCA (NMHC version) to study global changes in the oxidative capacity of natural environments.

II- Implementation of tropospheric halogens in LMDz-INCA

a - Schematic representation of the chemistry halogens



- Heterogeneous reaction
- Photolytic reaction
- Gaseous reaction
- Reaction involving iodine only
- Reaction involving bromine only
- Reaction involving chlorine only

Wet and Dry deposition

$HOBr$ HBr $BrNO_3$ $BrNO_2$ Br_2
HCl $HOCl$ $ClNO_3$ $ClNO_2$ Cl_2
HOI HI INO_3 INO_2 I_2 I_2O_x
$BrCl$ IBr ICl

Natural emissions

CH_3Br $CHBr_3$ CH_2Br_2
CH_3Cl $CHCl_3$ CH_2Cl_2 $ClNO_2$
HCl
I_2 HOI CH_3I CH_2I_2
CH_2IBr CH_2ICl

In total 135 reactions and 36 species were introduced to the chemical scheme in INCA.

II- Implementation of tropospheric halogens in LMDz-INCA

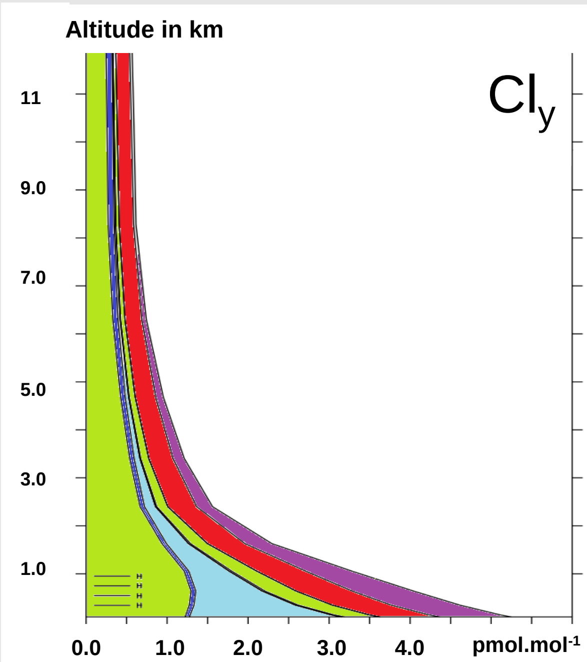
b – Emission fluxes considered and model setup

Species	Model emissions (Gg of halogen /yr)	Reference
CH_3Br	90.68	Schmidt et al., 2016
CH_2Br_2	54.6	Schmidt et al., 2016
$CHBr_3$	397.1	Schmidt et al., 2016
Sea salt release of IBr *	1239	Sherwen et al., 2016
CH_2IBr	19.18	Ordonez et al., 2012
Br_y	1801	
CH_3Cl	2329	Schmidt et al., 2016
CH_2Cl_2	479.6	Schmidt et al., 2016
$CHCl_3$	260	Schmidt et al., 2016
$ClNO_2$	658.7	Sherwen et al., 2016
CH_2ICl	39.04	Ordonez et al., 2012
Sea salt release of ICl *	6847	Sherwen et al., 2016
HCl	102 425	
Total Cl_y	112818	
CH_2IBr	30.46	Ordonez et al., 2012
CH_2ICl	139.8	Ordonez et al., 2012
I_2	317.7	Carpenter et al., 2013
HOI	2 889	Carpenter et al., 2013
CH_3I	242.7	Ordonez et al., 2012
CH_2I_2	107.5	Ordonez et al., 2012
Total I_y	3727	

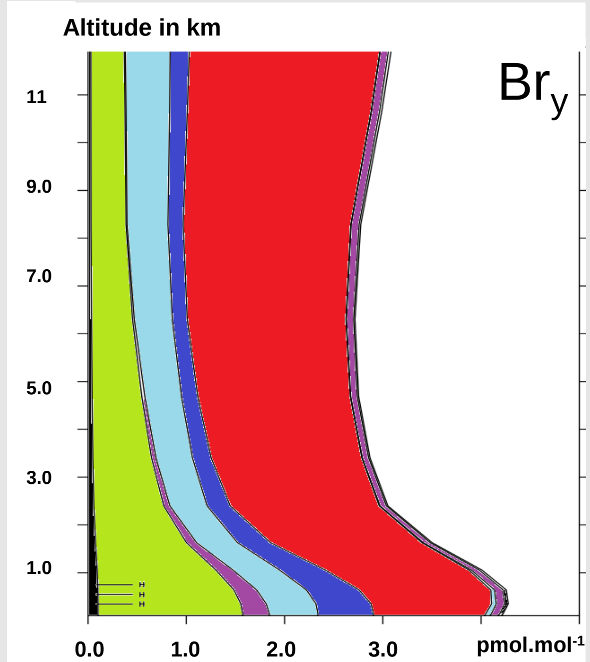
Next we present the **global annual average results** of a run for the year 2009.

III- Model results

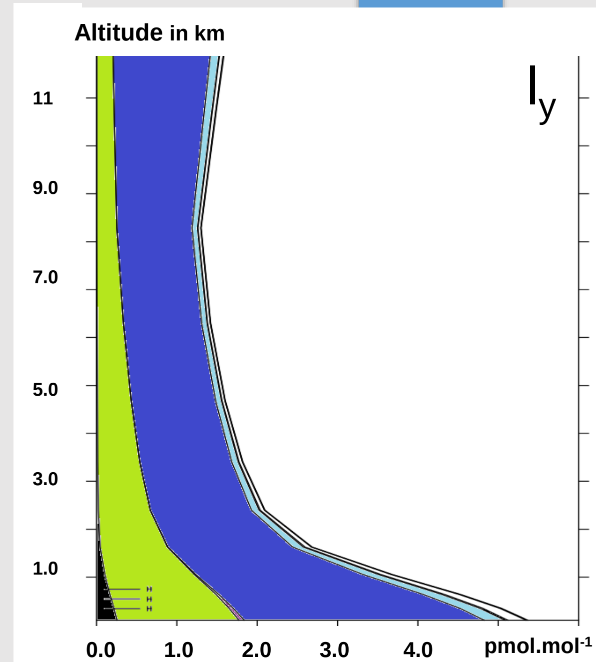
a- Vertical distribution of halogenated compounds



Color	Species
Light green	HOCl
Blue	$ClNO_3$
Light blue	$ClNO_2$
Black	ClO_2
Light green	Cl_2
Red	BrCl
Purple	ICl



Color	Species
Black	Br_2
Light green	BrCl
Purple	IBr
Light blue	HOBr
Blue	BrO
Red	HBr
Light blue	$BrNO_2$
Purple	$BrNO_3$
Black	Br

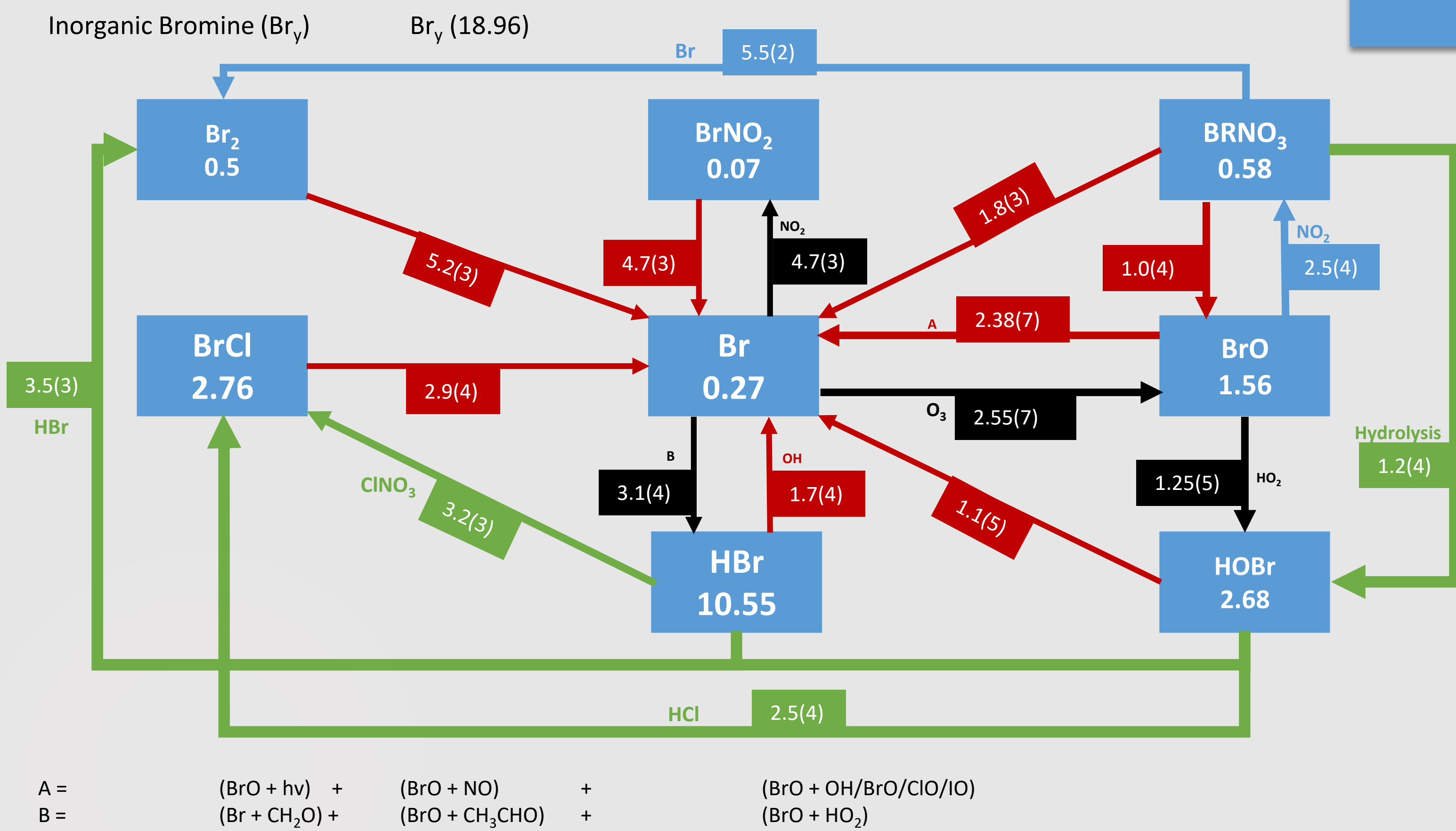


Color	Species
Black	CH_2IX
Light green	CH_3I
Purple	I_2
Blue	HOI
Light blue	IO
Black	OIO / HI / INO / INO_2
White	INO_3

Vertical concentration profiles are on the lower-end of the range found in other models (Sherwen et al., 21016b ; Badia et al., 2019).

III- Model results

b- Tropospheric budget and cycling of reactive bromine (Br_y)

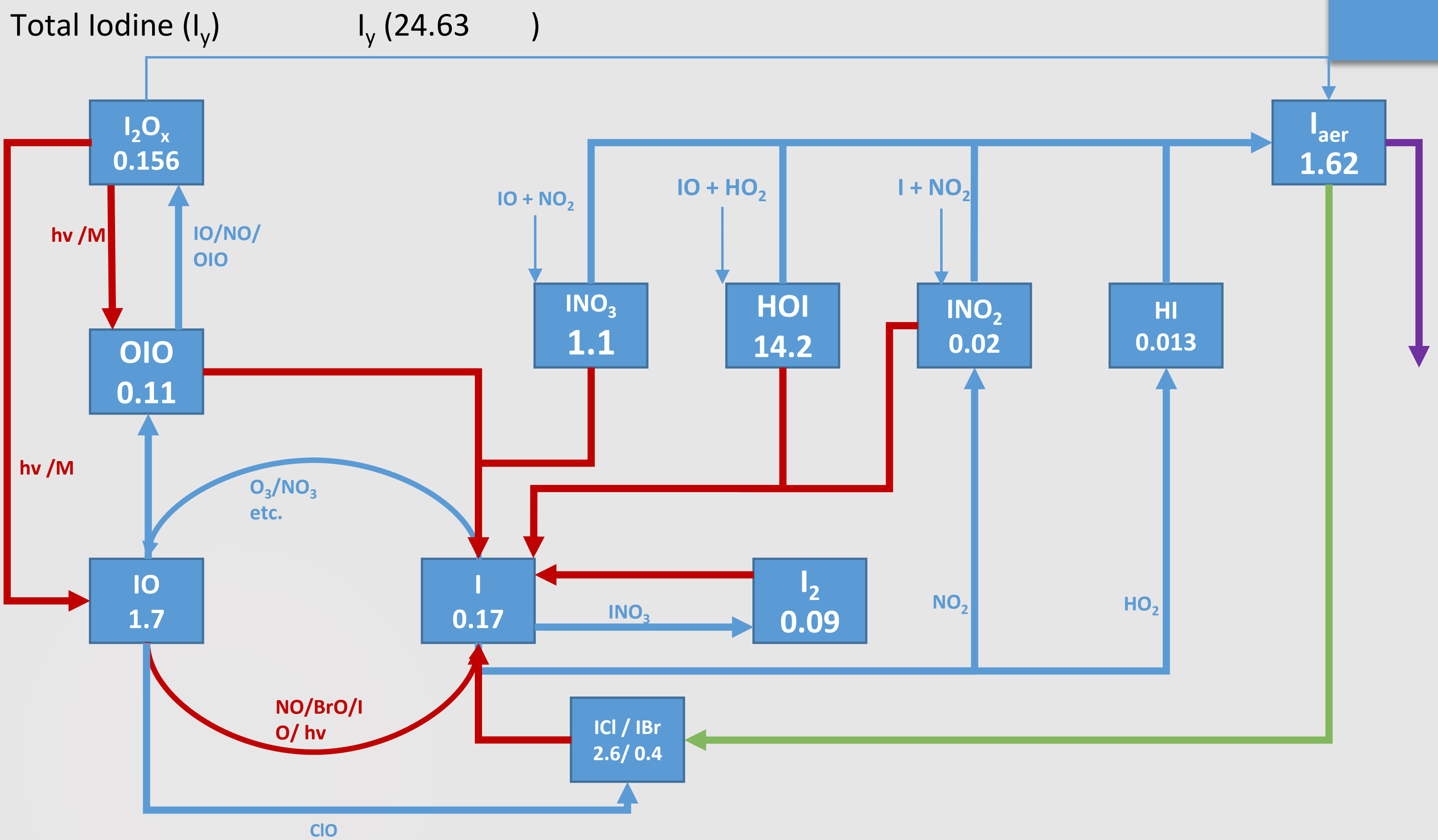


Rates are in Gg Br.yr^{-1}, masses in the boxes are in Gg Br. Read 5.8(4) as 5.8×10^4 Gg Br.yr^{-1}. Arrows in black are for gaseous reactions, red for photolysis and green for heterogeneous reactions taking place in seasalt and sulfate aerosol. Sources and sinks of total inorganic bromine are in orange.

⇨ Br_y budgets represent a lower limit compared to GEOS-Chem (Schmidt et al., 2016).

III- Model results

c- Tropospheric budget of reactive inorganic iodine (I_y)



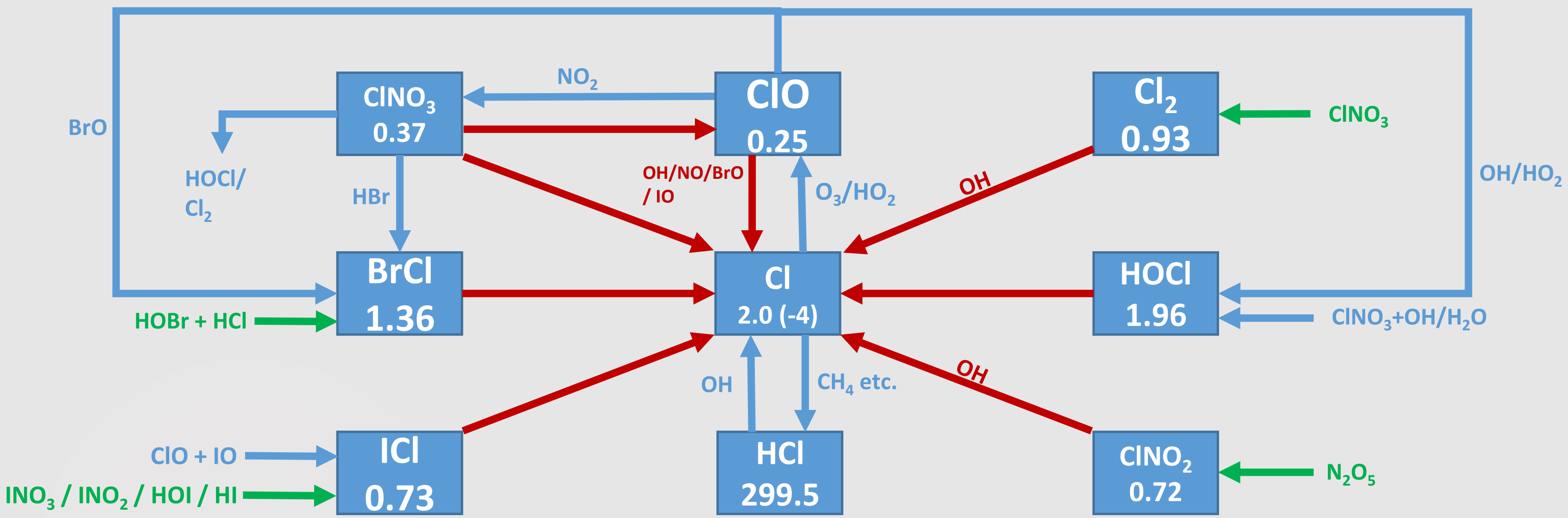
Masses in boxes are in Gg I. Red lines for photolysis; blue lines for chemical pathways; green lines for heterogeneous pathway; purple lines, depositional pathway.

➡ **I_y budgets represent a lower limit compared to GEOS-Chem (Sherwen et al., 2016a).**

III- Model results

d- Global budget and cycling of tropospheric chlorine (Cl_y)

Inorganic Chlorine (Cl_y) Cl_y (5)



Masses in the boxes are in Gg Br. Chemical pathways are in blue, photolysis reactions are shown in red and heterogeneous ones in green.

⇒ Cl_y budgets represent a lower limit compared to GEOS-Chem (Xuan Wang et al.,2019) since acid displacement reactions and many heterogeneous reactions are willingly not taken into account. Nevertheless, the chlorine cycle is active.

IV- Tropospheric impact of halogens

a - Ozone chemical loss

Global tropospheric O_x budgets of the "Halo" and "PRES" simulations in INCA :

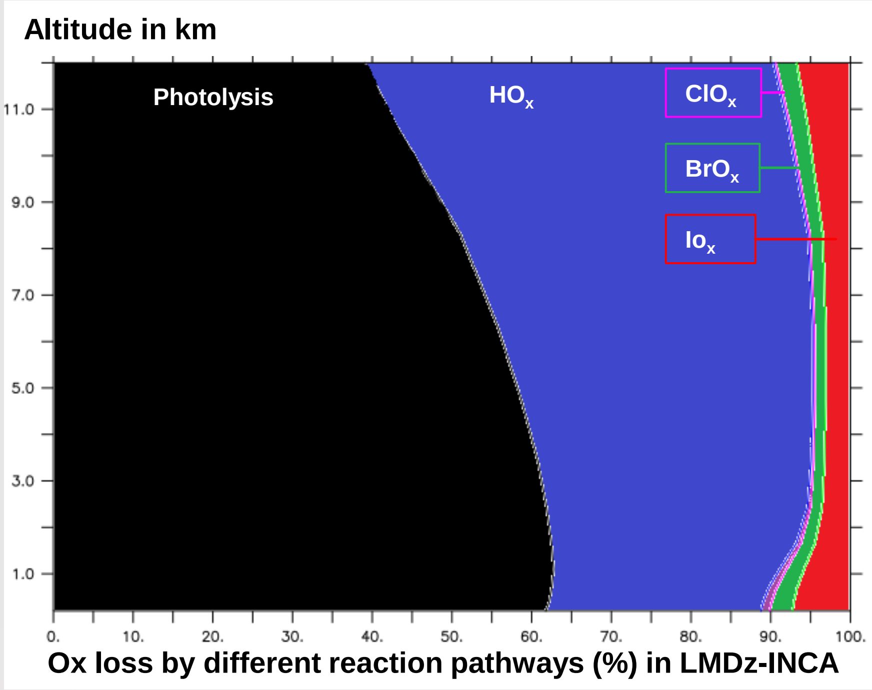
		Run with halogens	Run without Halogens	Delta
	O_x chemical sources (Tg O_3 /yr)			
O_x chemical sources (Tg O_3 /yr)	$NO + HO_2$	3075	3384	-309
	$NO + CH_3O_2$	1118	1174	-56
	$NO + RO_2$	675	664.2	10.8
	Total chemical O_x sources (PO_x)	**4868**	**5222**	**-354**
	O_x chemical sinks (Tg O_3 /yr)			
Main O_3 chemical sinks (Tg O_3 /yr)	$O_3 + H_2O \rightarrow 2\ OH + O_2$	2237	2416	-179
	$O_3 + HO_2 \rightarrow OH + O_2$	1141	1302	-161
	$O_3 + OH \rightarrow HO_2 + O_2$	409.3	493.3	-84
Bromine-driven O_3 chemical loss (Tg O_3 /yr)	$HOBR + hv \rightarrow Br + OH$	66		
	$HOBr + HCl \rightarrow BrCl$	15.2		
	$HOBr + HBr \rightarrow Br_2 + H_2O$ (aq. Aerosol)	1.1		
	Other bromine Ox sinks	6.5		
	Total bromine Ox sinks	**88.8**		
Iodine-driven O_3 chemical loss (Tg O_3 /yr)	$HOI + hv \rightarrow I + OH$	231.3		
	$OIO + hv \rightarrow I + O_2$	21.3		
	Other iodine Ox sinks	1.55		
	Total iodine Ox sinks	**254.2**		
Chlorine-driven O_3 chemical loss (Tg O_3 /yr)	$HOCl + hv \rightarrow Cl + OH$	10.0		
	Other chlorine Ox sinks	6.9		
	Total chlorine Ox sinks	**16.9**		
O_x loss (Tg O_3 /yr)	**Total chem. O_x sink (LO_x)**	**4147.2**	**4212**	**-70.8**
	Other O_x budgets			
Other O_x budgets	**O_3 burden (Tg)**	**282.6**	**329.8**	**-47.2**
	O_3 PO_x - LO_x (Tg O_3 /yr)	**720.8**	**1010**	**-289.2**
	O_3 dry deposition (Tg O_3 /yr)	**1037**	**1213**	**-176**
	O_3 lifetime (days)	**19.9**	**22.19**	**-2.29**
	O_3 STE (PO_x - LO_x - Dry dep) (Tg O_3 /yr)	**316.2**	**203**	**113.2**

➡ **Trends in O_x budget changes are similar to what other studies have reported (Saiz Lopez et al., 2012 ; Sherwen et al., 2016a,b ; Badia et al., 2019).**

➡ **Halogens account for 8.7% of total tropospheric O_3 loss but represent a lower-limit compared to results from other GCMs (21.4 % in GEOS-Chem (Sherwen et al., 2016b)).**

IV- Tropospheric impact of halogens

b – Changes in the oxidation capacity



In LMDz-INCA

- Tropospheric O_3 concentrations decrease by 14.3 % due to inclusion of halogens
- Oceanic surface O_3 concentrations decrease by 27 %
- OH surface concentrations decrease by 1.7 % on inclusion of halogens (Similar to Sherwen et al., 2016a)
- Methane lifetime increases from 8.2 years to 8.6 years (0.4 year)

In GEOS-Chem (Sherwen et al., 2016b)

- Tropospheric O_3 concentrations decrease by 18.6 % due to inclusion of halogens
- Oceanic surface O_3 concentrations decrease by 30 %
- OH surface concentrations decrease by 1.8 % on inclusion of halogens
- Methane lifetime increases from 7.47 years to 8.28 years (0.81 year)

V- Conclusion

- We have implemented the chemistry of halogens in LMDz-INCA
- Vertical distribution of inorganic halogens is reasonable
- As of today, LMDz-INCA consistently simulates the impact of halogens on the tropospheric oxidative capacity
- Considering the current set-up, the impact on O_3 and OH is on the lower end of the range of other models
- Perspectives :
  - Current organic and inorganic natural sources of tropospheric halogens will be improved (Collaboration with A. Saiz Lopez)
  - Chosen reactive uptake coefficients on aerosols and henry constants are not final

VI- Annex : Reactive uptake coefficients in LMDz-INCA

Reaction	Reactive uptake coefficient on sea salt (γ)	Reactive uptake coefficient on sulfate aerosols (γ)
$HOBr + HBr \rightarrow Br_2 + H_2O$	0.05	0.05
$HOBr + HCl \rightarrow BrCl + H_2O$	0.1	0.1
$ClNO_3 + HBr \rightarrow BrCl + HNO_3$	0.2	0.024
$ClNO_3 \rightarrow HOCl + HNO_3$	0.024	0.024
$BrNO_3 \rightarrow HOBr + HNO_3$	0.8 ou 0.3	0.8
$I_2O_x \rightarrow I_{aer}$	0.02	0.02
$HI \rightarrow I_{aer}$	0.1	
$HOI \rightarrow 0.85{*}ICl + 0.15{*}IBr + HNO_3$	0.01	
$INO_3 \rightarrow 0.85{*}ICl + 0.15{*}IBr + HNO_3$	0.01	
$INO_2 \rightarrow 0.85{*}ICl + 0.15{*}IBr + HNO_3$	0.02	

VI- Annex : Henry's law constants in LMDz-INCA

Species	Henry's law constant H at 298 K (M.atm-1)	d(lnH)/d(1/T) (K)	References
HOBr	1.90E+03	0	Sander (2015)
$BrNO_2$	3.00E-01	0	Frenzel et al. (1998)
$BrNO_3$	1.00E+20	0	Sander (2015)
Br_2	7.60E-01	3720	Dean (1992)
HOCl	6.50E+03	5900	Sander (2015)
BrCl	9.70E-01	0	Sander (2015)
ICl	1.11E+02	2110	Sander (2015) ; Sander et al. (2006)
IBr	2.43E+01	4920	Sander (2015) ; Sander et al. (2006)
HOI	1.53E+04	8370	Sander (2015) ; Sander et al. (2006)
HI	7.43E+13	3190	Sander (2015) ; Sander et al. (2006)
I_2	2.63E+00	7510	Sander (2015) ; Sander et al. (2006)
INO_2	3.00E-01	7240	Sander (2015) ; Sander et al. (2006)
INO_3	2.69E+15	39800	Vogt et al. (1999) ; Kaltsoyannis and Plane (2008
$ClNO_3$	2.69E+15	0	Vogt et al. (1999) ; Kaltsoyannis and Plane (2008
I_2O_2	2.69E+15	18900	Vogt et al. (1999) ; Kaltsoyannis and Plane (2008
I_2O_3	2.69E+15	7700	Vogt et al. (1999) ; Kaltsoyannis and Plane (2008
I_2O_4	2.69E+15	13400	Vogt et al. (1999) ; Kaltsoyannis and Plane (2008
I_{aer}	2.69E+15	39800	
Cl_2	8.60E-02	2000	Kavanaugh and Trussell [1980]
$ClNO_2$	2.40E-02	0	Sander (2015)
HCl	7.10E+15	5900	Sander (2015)
HBr	7.10E+13	10200	Frenzel et al. (1998), Schweitzer et al. (2000)