



**HARVARD**  
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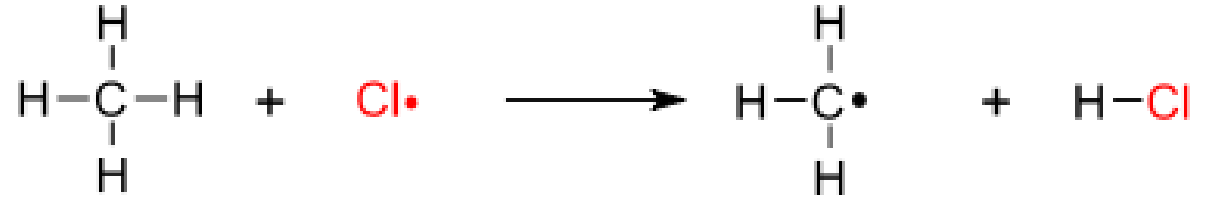
# Simulation of Inorganic Chloride and its Impact on Global Tropospheric Chemistry

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**Sebastian Eastham (MIT)**

# Inorganic Chlorine in Troposphere

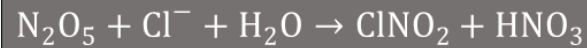
- Methane Oxidation



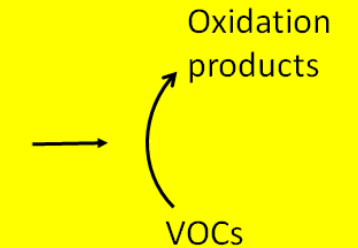
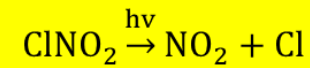
- Tropospheric Ozone

- $\text{ClNO}_2$

Nighttime:



Daytime:

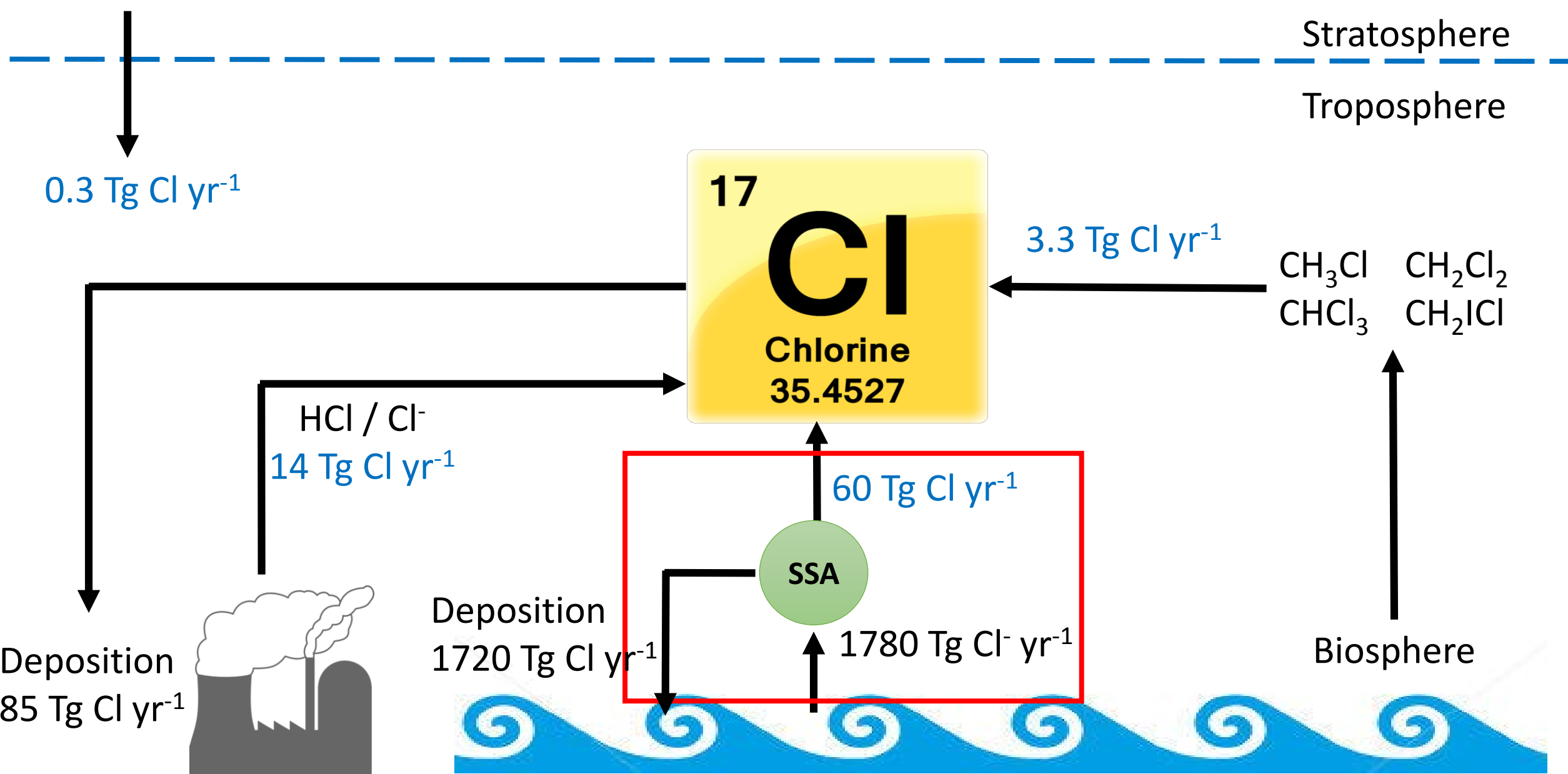


- Bromine and Iodine chemistry

- Mercury Oxidation

- Aerosol Composition

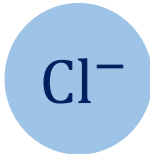
# Sources of Tropospheric Inorganic Chlorine



# Simulating Cl<sup>-</sup>: Alkalinity Titration and Thermodynamics

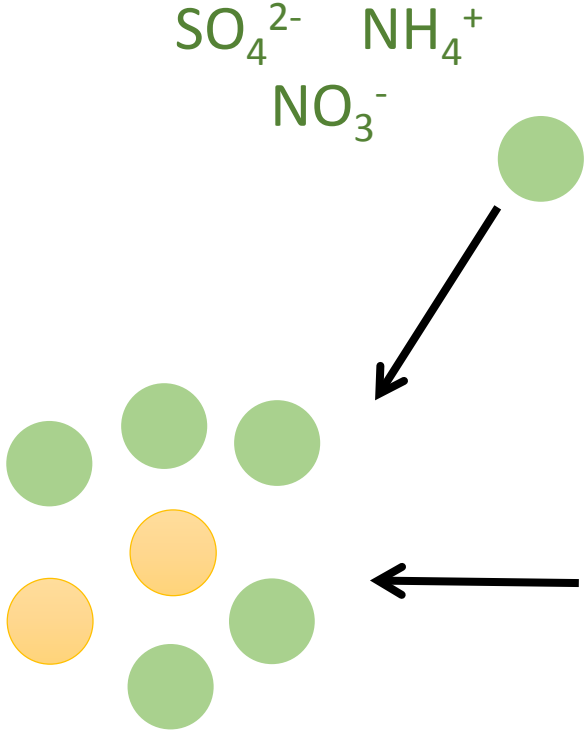
4 new species:  
Fine Cl<sup>-</sup>  
Coarse Cl<sup>-</sup>  
Fine Alkalinity  
Coarse Alkalinity

Fresh Sea Salt  
Aerosol  
w/ Alkalinity



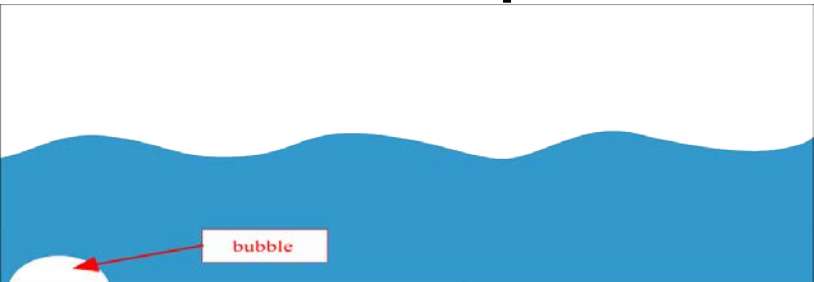
Acid gases  
CO<sub>2</sub>  
Alkalinity titration

Acidic or  
Neutralized  
Aerosol



Gases

NH<sub>3</sub> – HNO<sub>3</sub> – H<sub>2</sub>SO<sub>4</sub> – HCl  
Thermodynamics system

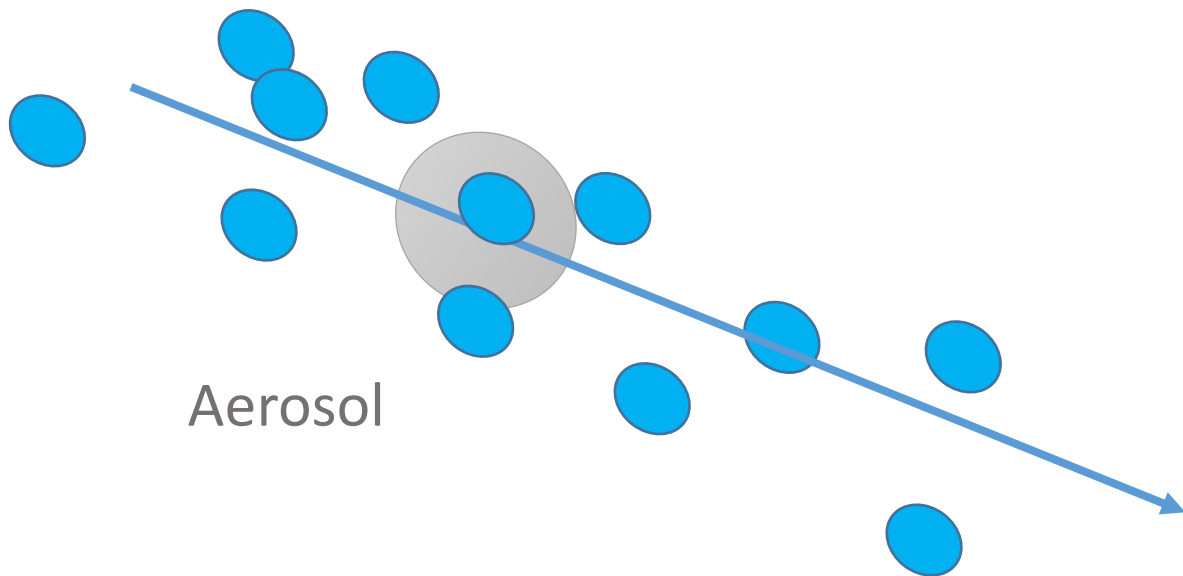


# Simulating Cl<sup>-</sup>: Thermodynamics

Fine mode

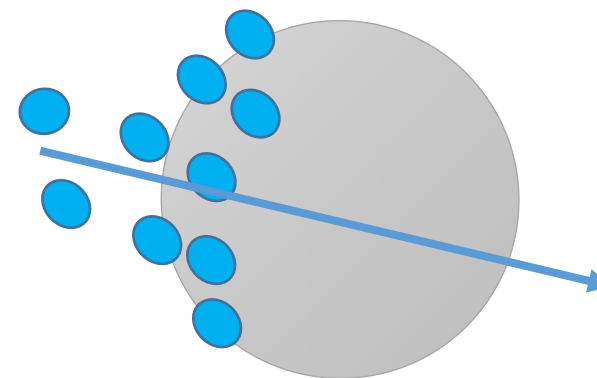
Fast equilibrium

Gas molecule



Coarse mode

Limited by mass transfer

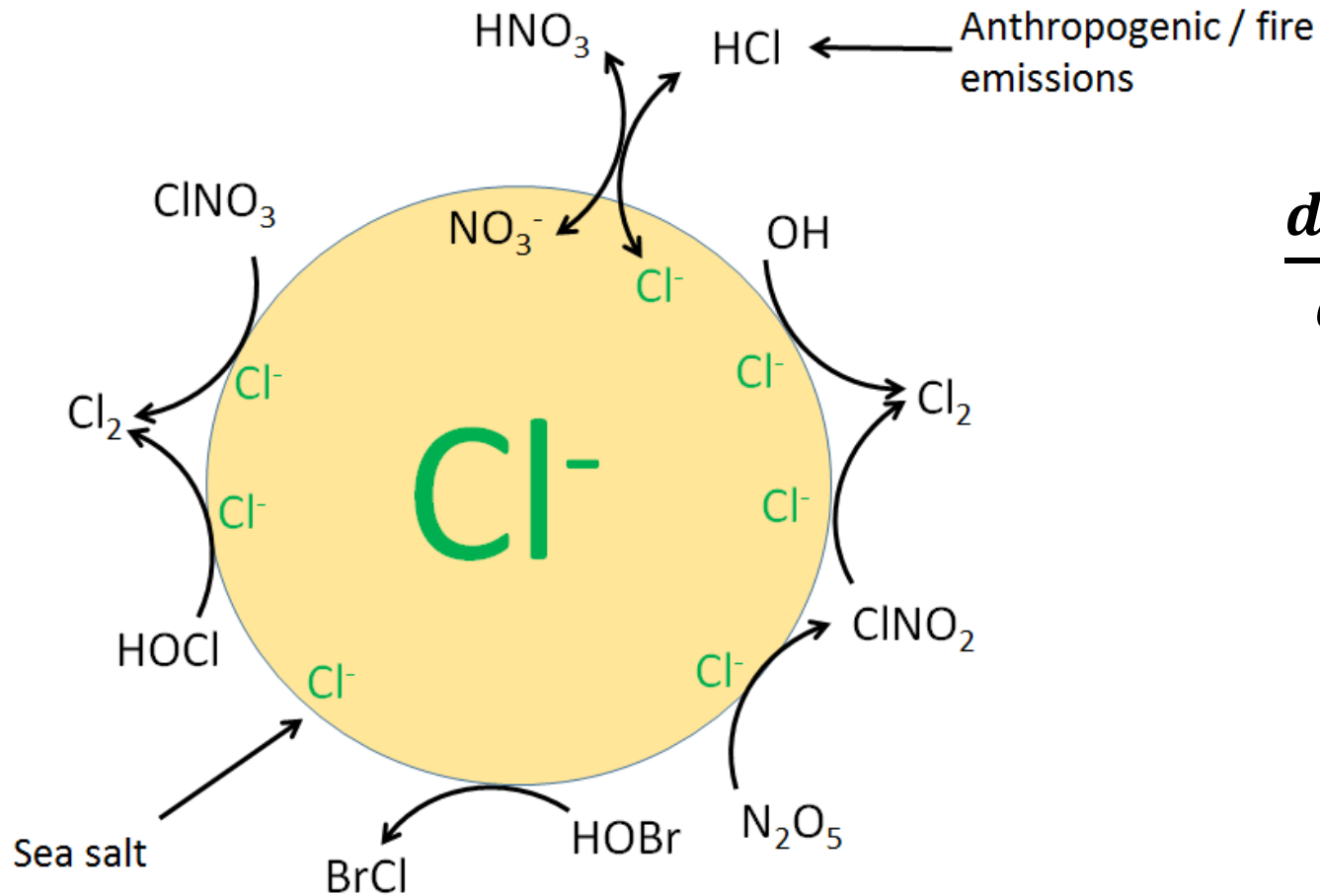


Dynamic approach:

$$Q = \frac{-\beta}{(D_{g,HNO_3} f(Kn, a_{HNO_3}) C_{HNO_3}^{eq} + D_{g,HCl} f(Kn, a_{HCl}) C_{HCl}^{eq}) \eta}$$

$$\beta = -D_{g,HNO_3} f(Kn, a_{HNO_3}) C_{HNO_3}^{eq} - D_{g,HCl} f(Kn, a_{HCl}) C_{HCl}^{eq} + \frac{\alpha}{2\pi D_p N}$$

# Simulating Cl<sup>-</sup> related Heterogeneous Chemistry



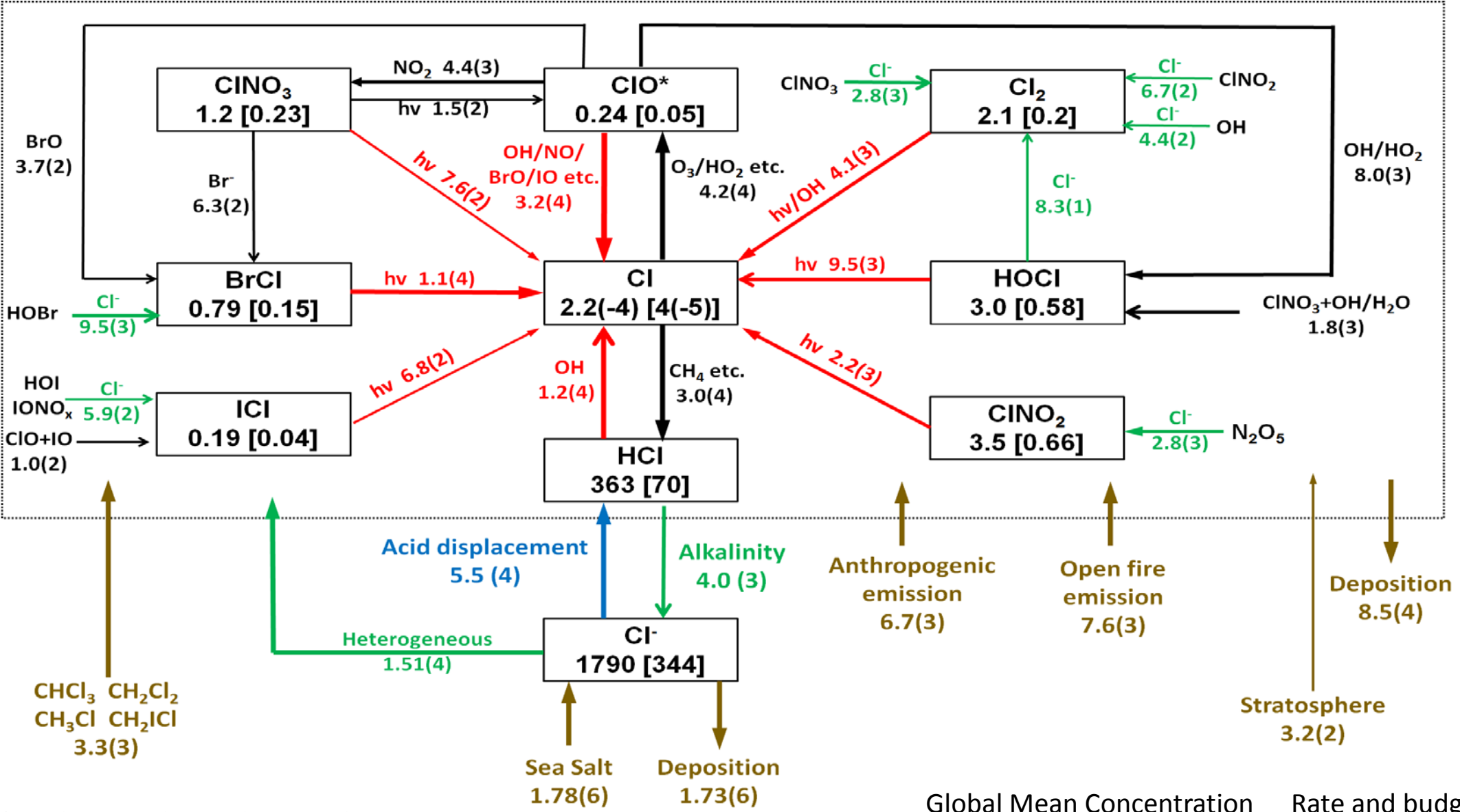
$$\frac{d[X]}{dt} = - \left( \frac{r}{D_g} + \frac{4}{c\gamma} \right)^{-1} [X][A]$$

Gas diffusion

Mass accommodation + chemistry processes

$$\gamma = \gamma([\text{Cl}^-])$$

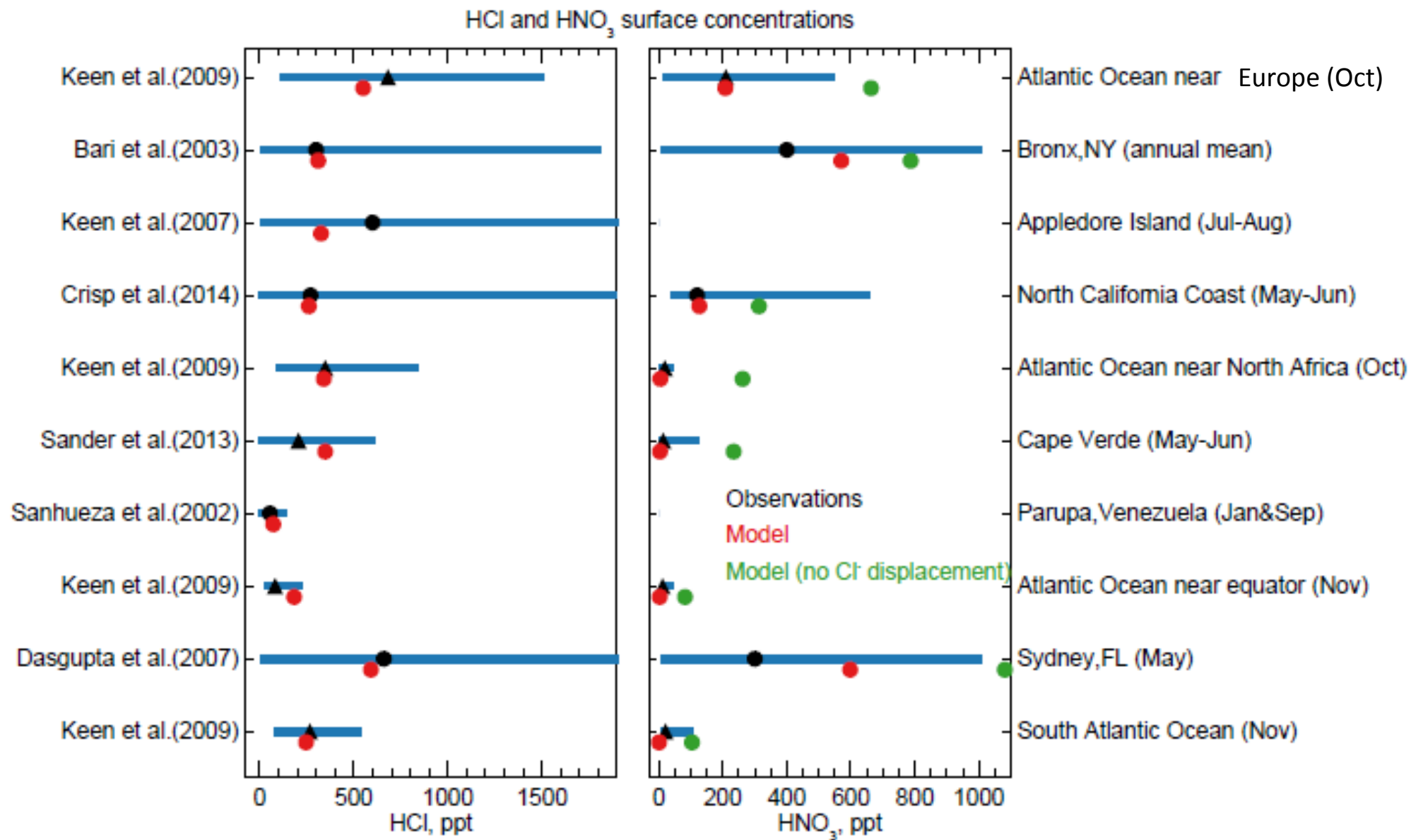
# Tropospheric Chlorine Simulation in GEOS-Chem



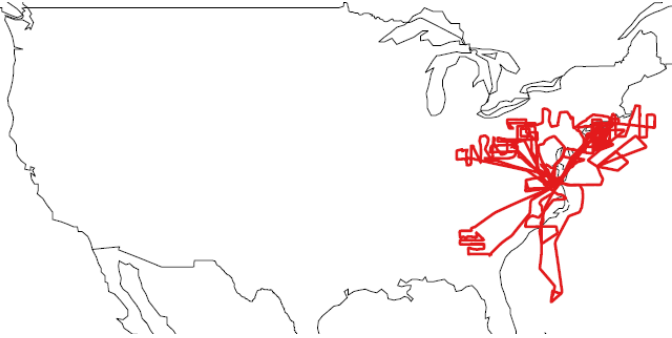
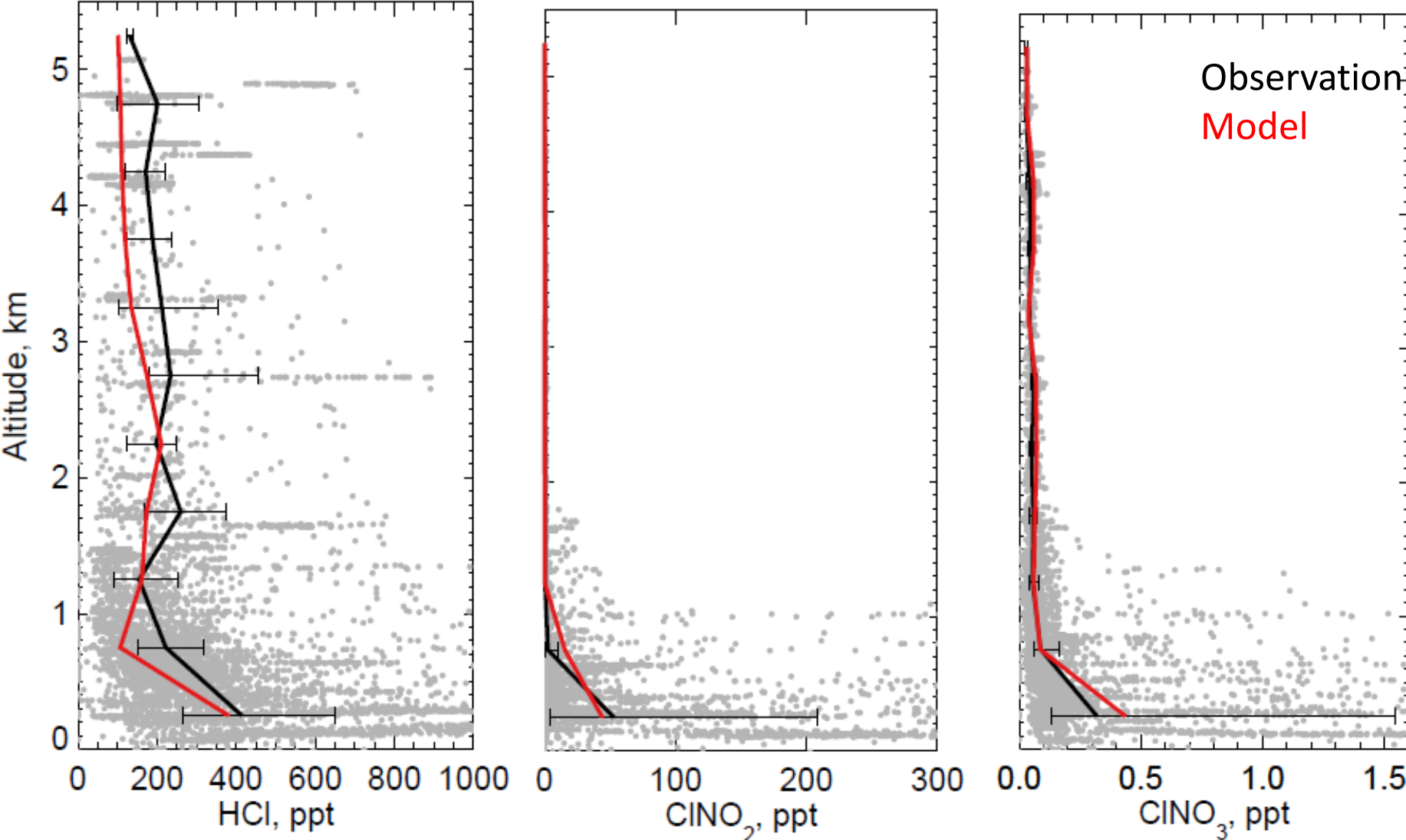
$\text{ClO}^*$  stands for  $\text{ClO} + \text{OCIO} + \text{ClO}_2 + 2\text{Cl}_2\text{O}_2$

Global Mean Concentration [70] = 70 ppt  
 Rate and budget 1.2 (4) =  $1.2 \times 10^4$  Gg/yr

# Comparison to Surface HCl and HNO<sub>3</sub> Observations



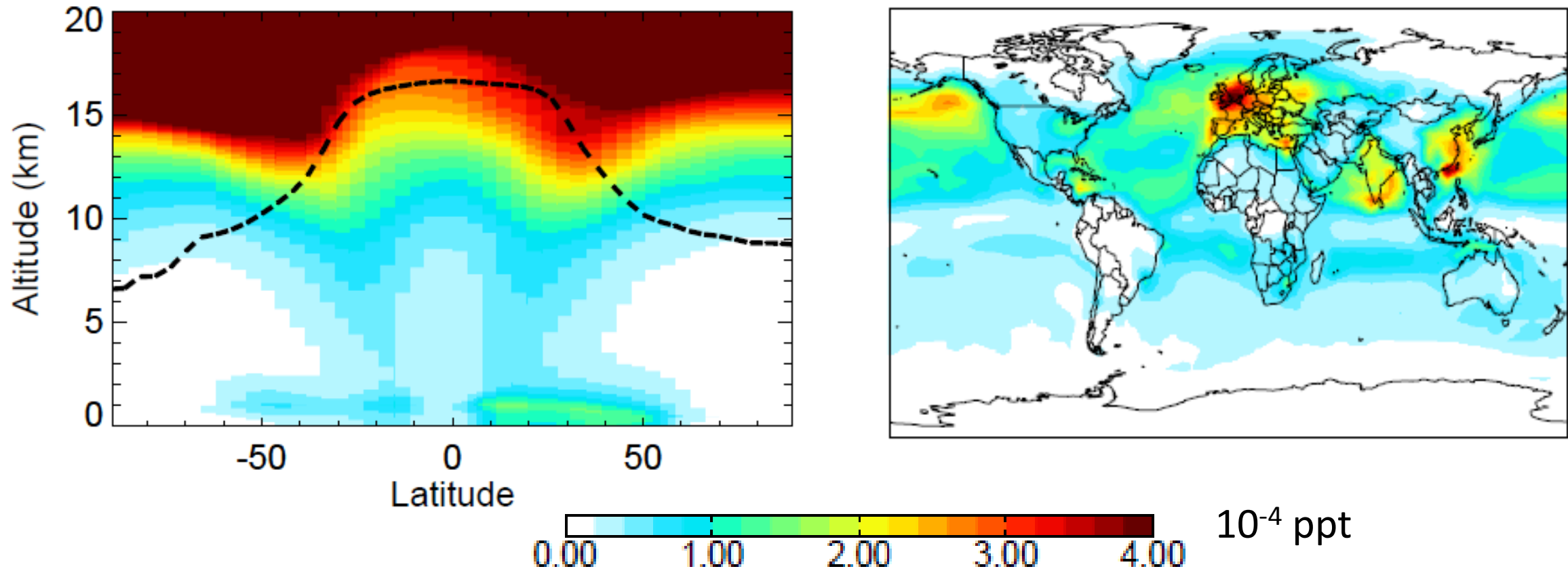
# Comparison to Aircraft Measurements



Feb – Mar 2015

# Impact on Cl atom and Methane Oxidation

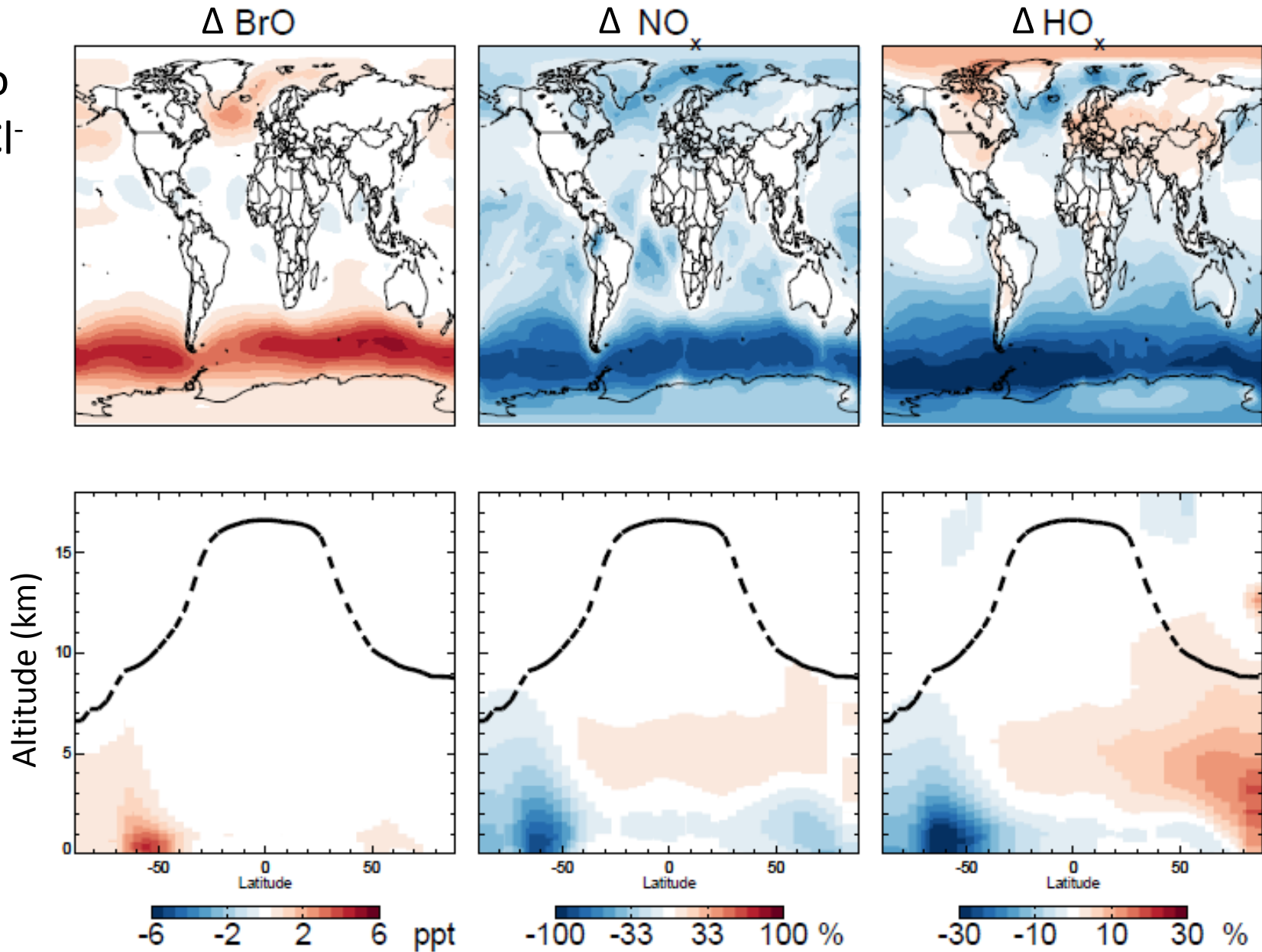
## Zonal (left) and surface (right) annual mean Cl atom concentrations



- Global tropospheric mean concentration:  $\sim 700 \text{ cm}^{-3}$ , within the range of that derived from  $\text{C}_2\text{Cl}_4$  measurements ( $500 - 1000 \text{ cm}^{-3}$ , Singh et al., 1996)
- Contributing 1.2% of tropospheric  $\text{CH}_4$  loss, with larger regional effect in the PBL (at most 25%)

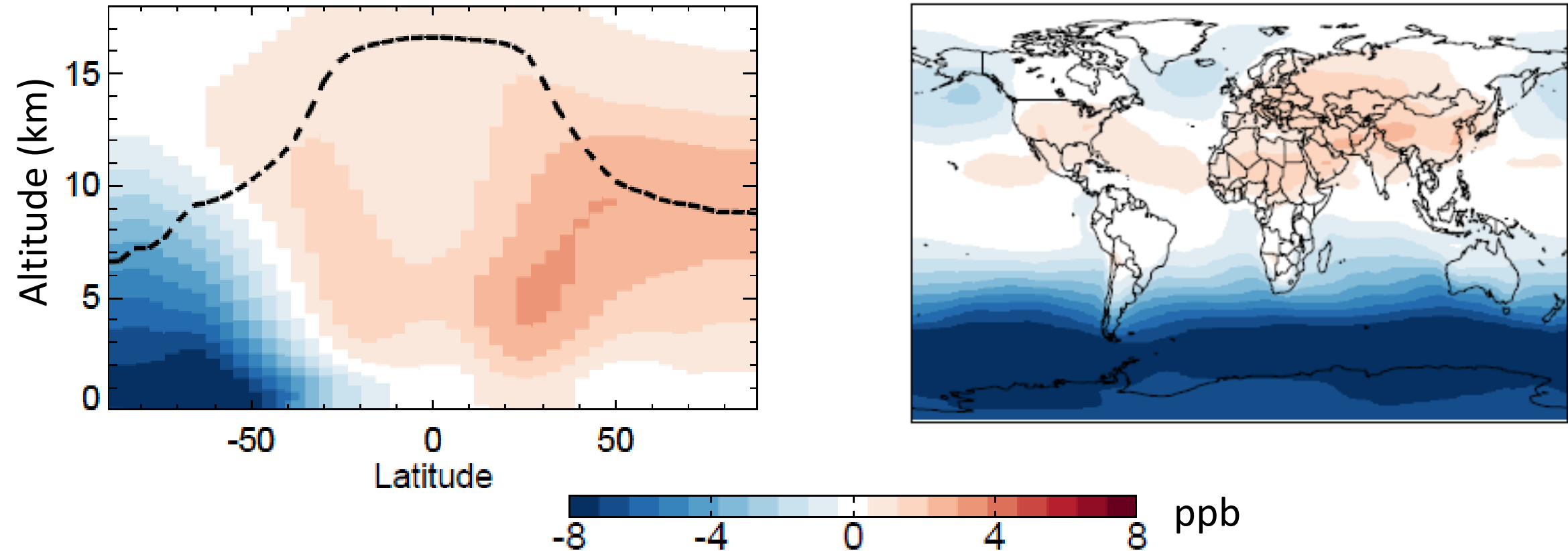
# Impact on Tropospheric Ozone

Change due to the updated Cl-chemistry



# Impact on Tropospheric Ozone

## Changes of O<sub>3</sub> due to updated Cl<sup>-</sup> chemistry



- Most impact of Cl<sup>-</sup> on O<sub>3</sub> is through its impact on Bromine chemistry.
- ClNO<sub>2</sub> chemistry accounts for up to 8 ppb increase of afternoon surface O<sub>3</sub> in polluted areas in winter, but < 1 ppb in summer.

Thank you!

*Presenting the whole story of chlorine chemistry  
needs much more than 10 minutes*

*just like*

*Running this new simulation takes a bit longer than  
present version of GEOS-Chem*