Tropospheric Chlorine Chemistry in GEOS-Chem

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Sources and Impact of Halogens in Troposphere

**Stratosphere**

- **Ozone destruction**
  \[ X + O_3 \rightarrow XO + O_2 \]

- **Methane destruction**
  \[ Cl + CH_4 \]

- **Heterogeneous cycling of halogens**

**Continents**

- **Ultrafine particle formation**
  \[ IO, OIO \rightarrow \text{Particle} \]

- **Oxidation of mercury**
  \[ Br + Hg \]

**Ocean**

- **Release of halogens from organic precursors**
  \[ \text{Org-X} + hv/OH \rightarrow X + \ldots \]

- **Organic halogens**

- **Sea salt**

**X = Cl, Br, I**
Simulating Chloride

4 new species:
- Fine Cl⁻
- Coarse Cl⁻
- Fine Alkalinity
- Coarse Alkalinity

Fresh Sea Salt Aerosol w/ Alkalinity

Acid gases → CO₂ → Acidic or Neutralized Aerosol

Alkalinity titration

Aerosol water / Cloud droplet

NH₃ → HNO₃ → H₂SO₄ → HCl

Thermodynamics system

SO₄^{2⁻} \text{ NH}_4^{+} \text{ NO}_3^{-}

ClNO₂, Cl₂, etc.

Gas molecule
Tropospheric Chlorine Chemistry

\[ \text{ClO}^* = \text{ClO} + \text{OCIO} + \text{ClO}_2 + 2\text{Cl}_2\text{O}_2 \]

Rate and mass \(1.2 \times 10^4\) Gg/yr

[60]: tropospheric average mixing ratio = 60 ppt
Global cycling of tropospheric chlorine

[60]: tropospheric average mixing ratio = 60 ppt

ClO* stands for ClO + OCIO + ClO2 + 2Cl2O2

Chlorine Model scheme in GEOS-Chem: 102 reactions

Rate and mass 1.2 (4) = 1.2 × 10^4 Gg/yr

ClO: tropospheric average mixing ratio = 60 ppt
Impact of Chlorine Chemistry on Oxidants

Net: $\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$

Net: $\text{ClO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$

Net: $\text{HOBr(aq)} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$
Regional Analysis ---- Northeastern US Winter

Feb – Mar 2015

Mean diurnal variation of HCl & ClNO₂ below PBL

- ClNO₂ chemistry accounts for ~ 6ppb of afternoon O₃ in eastern US.
- Adding anthropogenic chlorine (Lee et al., 2018) does not change the results much.

Measurement data are provided by Joel Thornton’s group at UW
Anthropogenic Chlorine in China

Anthropogenic Chlorine Emission in China

- HCl and Cl⁻ emission (Fu et al., 2018) including:
  - Coal burning
  - Waste incineration
  - Industrial processes
  - Biomass burning

- Cl⁻ from anthropogenic dust
  - Derived from MEIC inventory and Reff et al. (2009).

- CHCl₃ emission based on Fang et al. (2018).

- CH₂Cl₂ emission based on Feng et al. (2018).
Impact of Anthropogenic Chlorine in China

Annual mean $\Delta \text{NO}_x$ (%)  
Annual mean $\Delta \text{O}_3$ (ppb)  
Annual mean $\Delta \text{OH}$ (%)  
Annual mean PM2.5 (%)
Impact of Chlorine

Global:
- $\text{O}_3$: 7%
- OH: 3%
- BrO: 85%
- CH$_4$ loss: 2%
- C$_2$H$_6$ loss: 20%

Regional:
- $\text{O}_3$
- ClNO$_2$: Up to 8 ppb
- Marine NO$_3^-$
- Important anthropogenic contribution in China.

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