Global tropospheric halogen chemistry and its impacts on ozone, OH, and aerosol concentrations

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GEOS-Chem global model includes comprehensive stratospheric+tropospheric Cl+Br+I chemistry

Long-standing collaboration between U. York, U. Washington, MIT, Harvard

![Diagram showing the interaction of various environmental factors such as industry, fires, volcanoes, plankton, halocarbons, hv, OH, halogen radicals, reservoirs, ozone, OH, sea-salt aerosol (SSA), and mercury.]
Global cycling of tropospheric chlorine in GEOS-Chem

Global masses (Gg), mixing ratios [ppt], rates (Gg a\(^{-1}\))

Read a(b) as a x 10\(^{b}\)

Wang et al. [ACP 2019]
Global distribution of HCl and Cl atoms

Annual mean GEOS-Chem concentrations

- HCl is highest over polluted oceans (acid displacement)
- Global mean tropospheric $[\text{Cl}] = 620$ atoms cm$^{-3}$; 1% of methane oxidation, 20% of ethane oxidation

Wang et al. [ACP 2019]
Importance of SSA acid displacement for low HNO₃ in marine air

HCl and HNO₃ in marine/coastal air

HNO₃ overestimate in remote air is a long-standing problem in global models; SSA acid displacement is part of solution

Wang et al. [ACP 2019]
Annual mean PM$_{2.5}$ chloride at US surface sites

Contours = model; circles = IMPROVE PM$_{2.5}$ observations (2016)

Model fine Cl$^-$ (<1 μm diameter)  Total Cl$^-$

- Aerosol chloride over US can be mainly explained by marine sources except in Southwest (dust)
- Mass transfer through HCl displaces marine Cl$^-$ from coarse to fine aerosol and enables transport inland
- Fine Cl$^-$ of marine origin over land has lost its association with Na$^+$

Wang et al. [ACP 2019]
Reactive chlorine over eastern US and downwind: WINTER aircraft observations

Mean concentrations below 1 km altitude vs. time of day

- HCl and ClNO₂ properly accounted for in model (also elsewhere)
- Cannot make sense of HOCl and Cl₂ observations

Wang et al. [ACP 2019]
Chlorine-driven changes in tropospheric chemistry

- Chlorine is a major source of BrO through HOBr + Cl\textsuperscript{-} heterogeneous reaction
- ClNO\textsubscript{2} chemistry increases NO\textsubscript{x} and ozone in polluted regions
- Global OH and ozone decreases not inconsistent with observations

*Wang et al. [ACP 2019]*
Anthropogenic chlorine in China

Large anthropogenic sources from biofuel, incineration, coal...

...are necessary in GEOS-Chem to reproduce observed ClNO$_2$

Fu et al. [2018]

Wang et al., in prep.
PM$_{2.5}$ enhancement from anthropogenic HCl emissions

Change in annual mean PM$_{2.5}$ in GEOS-Chem

Significant increase in overall PM$_{2.5}$, decrease in nitrate (which is too high in models)

Wang et al., in prep.
Conclusions

• Global source of tropospheric chlorine radicals driven mainly by sea-salt aerosol: (1) acid displacement followed by HCl + OH, (2) heterogeneous chemistry converting SSA Cl\(^-\) to BrCl, Cl\(_2\), ICl, ClNO\(_2\)

• Acid displacement drives high HCl concentrations in marine polluted air and depletes HNO\(_3\)

• High daytime Cl\(_2\) and HOCl in WINTER cannot be reconciled with model

• Most of the chlorine over the US is of marine origin, not so in China; anthropogenic chlorine in China makes significant contribution to PM\(_{2.5}\)

• Global mean tropospheric [Cl] = 620 atoms cm\(^{-3}\): 1% of methane sink, 20% of ethane sink

• Chlorine drives bromine chemistry through HOBr+Cl\(^-\) reaction and thus indirectly depletes ozone and OH