Tropospheric HO$_x$: controls and distribution

1. HO$_x$ sources, interconversion, and loss
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4. The NO$_x$-dependence of HO$_x$
5. Diurnal HO$_x$ cycles
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1. Tropospheric HO\textsubscript{\textit{x}}: sources, interconversion, loss

**HO\textsubscript{\textit{x}} sources:**
- everywhere: ozone photolysis \( O^1D + H_2O \rightarrow 2OH \)
- polluted air: HONO photolysis
  - formaldehyde photolysis
- upper troposphere: acetone photolysis

**OH \rightleftharpoons HO\textsubscript{2} interconversion:** ie. what controls the OH:HO\textsubscript{2} ratio?
- \( OH \rightarrow HO\textsubscript{2} \) via reaction with: CO, CH\textsubscript{4} (and other VOC’s), \( O_3 \) (important in clean air), \( SO_2 \) (in very polluted air)
- \( HO\textsubscript{2} \rightarrow OH \) via reaction with NO, \( O_3 \)

**HO\textsubscript{\textit{x}} destruction:**

**HO\textsubscript{\textit{x}} self reactions:** \( HO\textsubscript{2} + HO\textsubscript{2} \xrightarrow{M} H_2O_2 \)
\( OH + NO_2 \xrightarrow{M} HNO_3 \)

\( H_2O_2 \) and HNO\textsubscript{3} will photolyze if not removed by heterogeneous processes
2. HO$_x$ cycling – a case study from rural Germany

Concentrations and reaction rates controlling OH and HO$_2$ (Ehhalt et al., 1991). Concentrations are given in boxes (molecules cm$^{-3}$). rates are given on arrows (molecules cm$^{-3}$ s$^{-1}$).

Conditions for Deuselbach, Germany (May 20, 1983; 09:00-11:00).
3. HO_x lifetimes

**OH lifetimes:**

\[ \text{OH} + \text{CO} \rightarrow \text{HO}_2 \quad \tau_{\text{OH}} = \frac{3.9 \times 10^6}{9 \times 10^6} = \sim 0.4 \text{ s} \]

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \quad \tau_{\text{OH}} = \frac{3.9 \times 10^6}{1.8 \times 10^6} = \sim 2.2 \text{ s} \]

\[ \frac{2.2}{0.4} = 5 \]  On average, OH recycles through HO_2 five times before it is removed as HNO_3

**HO_2 lifetimes:**

\[ \text{HO}_2 + \text{NO} \text{ (and O}_3 \text{)} \rightarrow \text{OH} \quad \tau_{\text{HO}_2} = \frac{8.2 \times 10^7}{9 \times 10^6} = \sim 9 \text{ s} \]

\[ \text{HO}_2 + \text{HO}_2 \text{ (and OH)} \rightarrow \text{H}_2\text{O}_2 \text{ (and H}_2\text{O }) \quad \tau_{\text{HO}_2} = \frac{8.2 \times 10^7}{1 \times 10^5} = \sim 820 \text{ s} \]

**Overall HO_x lifetime:**

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \]

\[ \text{HO}_2 + \text{HO}_2 \text{ (and OH)} \rightarrow \text{H}_2\text{O}_2 \text{ (and H}_2\text{O }) \]

\[ \tau_{\text{OH}} = \frac{8.6 \times 10^7}{(1.8 \times 10^6 + 0.1 \times 10^6)} = \sim 45 \text{ s} \]
4. \( \text{HO}_x \) and \( \text{NO}_x \)

What happens if we remove \( \text{NO}_x \) from the system?

1. Short-term responses
   - \( \text{HO}_2 + \text{NO} \) slows
   - \( \text{HO}_2 + \text{O}_3 \) major \( \text{HO}_2 \) recycling mechanism
   - \( \text{HO}_2 \) and \( \text{HO}_x \) lifetimes increase
   - \( \text{OH}/\text{HO}_2 \) ratio decreases, \( \sim 1:100 \)
   - \( \text{NO}_x \) lifetime increases

2. Longer term responses
   - \( \text{O}_3 \) production slows so \( \text{O}_3 \) levels decline
   - \( \text{O}^{1}\text{D} \) production slows so \( \text{HO}_x \) production slows

These effects tend to offset "buffering" atmospheric \( \text{OH} \).
5. Diurnal cycling of HO\textsubscript{X}

note: log scale, OHx10

HO\textsubscript{X} production driven by photolysis

HO\textsubscript{X} lifetime is short, so levels track daily variations in sunlight.

OH daytime max $\sim 1\text{-}2 \times 10^6$ molecules cm\textsuperscript{-3}

HO\textsubscript{2} daytime max $\sim 5 \times 10^8$ molecules cm\textsuperscript{-3}

$$\frac{HO_2}{OH} > 100$$

Logan et al., 1981

Global photochemical model simulates: emissions, transport, radiation, chemistry

- OH maximum in tropics ($hv, H_2O$)
- $OH_{NH} > OH_{SH}$ ($NO_x, O_3$)
- Small range (~factor of 10)
- Avg. $OH \sim 1 \times 10^6$ molec cm$^{-3}$
7. What controls atmospheric OH?

**NOTE:** OH reacts with a HUGE number of chemicals in the atmosphere and controls the atmospheric levels of many of them.

**HOWEVER:** Few of these compounds control the abundance or lifetime of OH (or HO$_x$). Most just respond to OH levels.

Compounds that both affect and respond to OH levels cause feedbacks in the photochemical system.

These are: CO, CH$_4$ (NMHC’s), and NO$_x$. 
“for the 60 year period 1950-2010, where tropospheric methane concentration was fixed to increase by 1.5% annually, an average emission increase of only 1.05% per year was required…. due to the suppression of OH as methane goes up.”

“increasing methane by 1.5% per year caused an increase in $O_3$ of 0.45%, while OH concentration dropped by about 0.4% annually.”

increasing CO causes slight decrease in OH (due to $CO + OH \rightarrow O_2 CO_2 + HO_2$)

increasing $NO_x$ causes increase in $O_3$ and OH (due to $NO + HO_2 \rightarrow NO_2 + OH$)

OH roughly constant with increasing emissions of CO, $NO_x$, NMHC’s, and methane because the methane and $NO_x$ effects cancel out. If $NO_x$ is then decreased OH will decrease and methane will rise!