Global tropospheric OH

1. Global OH models
2. How can we estimate global OH?
3. What makes a good OH tracer?
4. $^{14}$CO
5. Methyl chloroform (CH$_3$CCl$_3$)

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

- OH maximum in tropics \((h, H_2O)\)
- \(\text{OH}_{\text{NH}} > \text{OH}_{\text{SH}}\) \((\text{NO}_x, \text{O}_3)\)

Small range (~factor of 10)

Avg. \(\text{OH} \sim 1 \times 10^6 \text{ molec cm}^{-3}\)
2. How can we estimate global OH?

1. run global OH models alone – validity depends on model parameterizations and input fields

2. compare *in situ* OH measurements with models
   - benefits – direct comparison
   - limitations - OH is hard to detect and calibrate
     - need many additional measurements (VOC’s) for direct comparison with models, so can only do in few places/times
     - useful for process studies to validate models, not useful for capturing global OH

3. use “tracers” to estimate the reactivity of the actual atmosphere
   - examples: $^{14}$CO and CH$_3$CCl$_3$
3. What makes a good tracer for OH?

1. well-known emission rate
2. can be measured precisely and accurately
3. well-known rate constant with OH
4. OH is the only sink
5. lifetime is long relative to transport

The perfect tracer would be a synthetic compounds released into the atmosphere intentionally, like fully deuterated methane - CD$_4$!

Sadly, that is not practical, so we take advantage of cosmogenic and unintentional anthropogenic tracers.
4. $^{14}\text{CO}$

**Stratosphere/Upper Troposphere**

- Cosmic ray protons + air → thermalized neutrons
  
  $^1n + ^{14}N \rightarrow ^{14}C + 1p$ (ie. $^{14}\text{N}(n,p)^{14}\text{C}$)
  
  $^{14}C + O_2 \rightarrow ^{14}CO + O$

- Transport

- $^{14}CO + OH \rightarrow H + ^{14}CO_2$

- $\tau_{^{14}CO} = 2-3$ months

$^{14}C$ production: 1.6-2.0 molecules s$^{-1}$ cm$^2$ (13-16 kg yr$^{-1}$) - varies with solar cycle

Recycled “biogenic” $^{14}C$ from soils/plants ~ 25% total $^{14}CO$ production

$^{14}C$ spontaneously decays by beta decay

$^{14}_{\text{C}} \rightarrow ^{14}_{\text{N}} + e^- + \bar{\nu}_e$

with $\tau_{1/2} = 5,715$ years (slow!)

$^{14}CO$ reflects OH levels in the atmosphere

If we know the production rate of $^{14}CO$, and the rate constant for loss via OH, we can measure atmospheric $^{14}CO$ and infer atmospheric OH.
5. What would a $^{14}$CO box model look like?

\[
\frac{\partial [^{14}CO]}{\partial t} = \frac{P}{V_{atm}} - k[^{14}CO]
\]

where: 
\[
P = \text{global production rate of } ^{14}CO \text{ (molecules s}^{-1}\text{)}
\]
\[
k = k_{OH} \times [OH_{avg}]
\]

actual measurements look like this:

note: low concentration!
summer low, winter high
reasonable agreement with model
5. Calculating global average OH from the methyl chloroform budget

CH$_3$CCl$_3$ industrial solvent (no natural sources)
atmospheric loss to OH, lifetime 5.5 years
average mixing ratio around 100 ppt
5b. Atmospheric CH$_3$CCl$_3$ observations

Northern hemisphere mid/high latitude sites

Northern hemisphere tropics

Southern hemisphere tropics

Southern hemisphere mid/high latitudes

Monthly mean observations from NOAA/CMDL and ALE/GAGE/AGAGE networks
Calculate hemispheric average OH, given the following:

- global CH$_3$CCl$_3$ production rate = 5.8 x 10$^{11}$ g/yr
- northern hemisphere emissions are 95% of total emissions
- $k_{OH} = 1.8 \times 10^{-12} \exp(-1550/T)$ cm$^3$ molec$^{-1}$ s$^{-1}$
- average tropospheric temperature = 277 K
- $k_{interhemispheric\ exchange} = 1$ yr$^{-1}$
- Northern hemisphere CH$_3$CCl$_3$ = 150 pptv
- Southern hemisphere CH$_3$CCl$_3$ = 130 pptv
- moles of air in the troposphere = 1.8 x 10$^{20}$