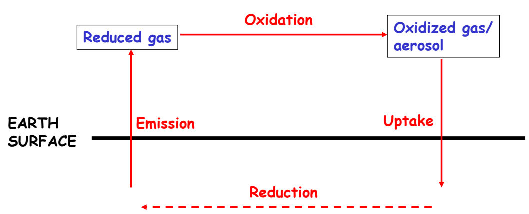
Tropospheric Chemistry

READING: Chapter 11 of text

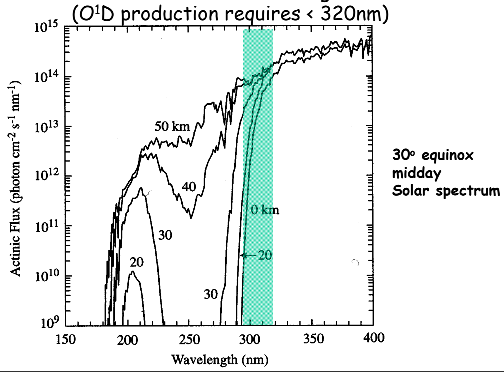
- Tropospheric OH source and sinks (CO and CH_4)
- Sources and Sinks of the OH sinks: CO and CH_4
- Stayin Alive: The OH Titration Problem

The Atmosphere: Oxidizing Medium



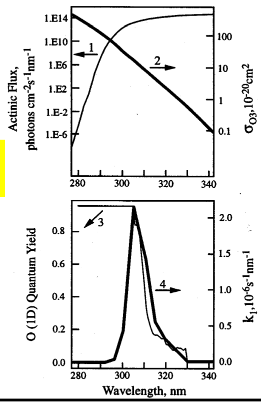
$O(^1D)$ Production in Troposphere?

Actinic Flux vs wavelength
(O^1D production requires < 320nm)

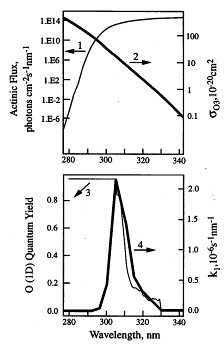


O(^{1}D) production in the Troposphere?

$$j_{O3} = \int_{\lambda} \phi(\lambda)\sigma(\lambda)I(\lambda)d\lambda$$



OH Radical: Main Tropospheric Oxidant



Primary source:

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (1)

$O(^1D) + M \rightarrow O + M$ (2)

$O(^1D) + H_2O \rightarrow 2OH$ (3)

Sink: oxidation of reduced species

$CO + OH \rightarrow CO_2 + H$

$CH_4 + OH \rightarrow CH_3 + H_2O$

} Major OH sinks *globally*

$HCFC + OH \rightarrow H_2O + \ldots$

GLOBAL MEAN [OH] = 1.0×10^6 molecules cm^{-3}

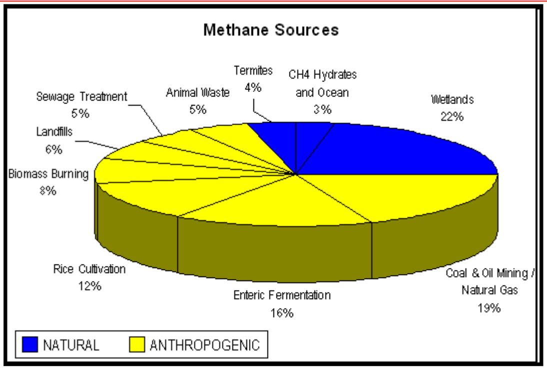
Questions

1. How would a thinning of the stratospheric ozone layer affect the source of OH in the troposphere?

2. How would adding sulfur to the stratosphere for geo-engineering affect the tropospheric OH source?

3. How might global warming affect the source rate of OH in the troposphere?

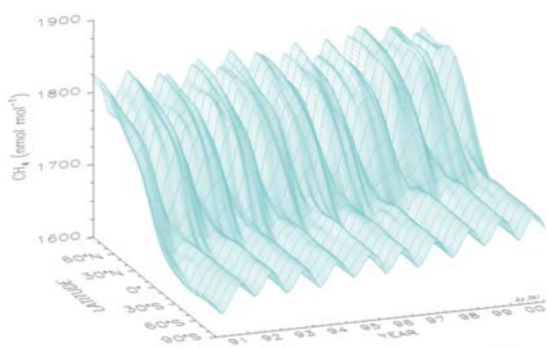
Global Sources of Methane



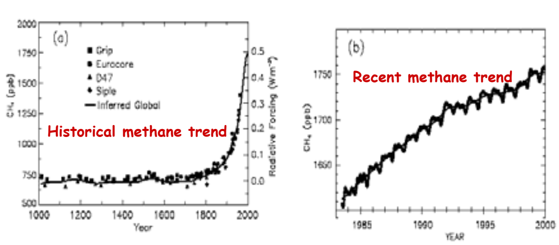
Augenbraun, et al, NASA GISS 1997 Global Methane Inventory.

Global Distribution of Methane

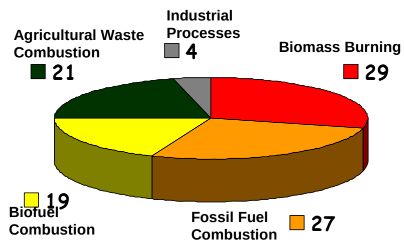
NOAA/CMDL surface air measurements



Historical Trends In Methane



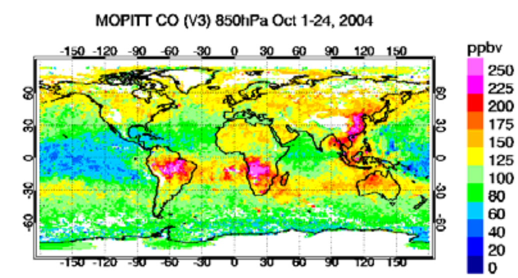
Global Sources of CO



Based on Olivier, et al *Chemosphere* 1999

Satellite Measurements

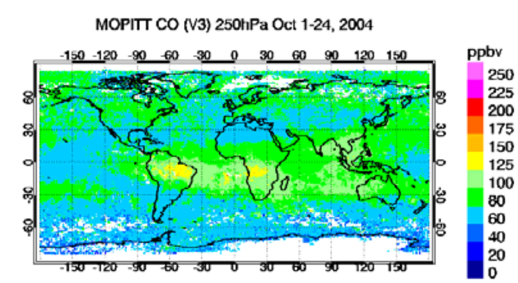
Lower Tropospheric CO



Gridded at 1x1deg from MOP02-200410??-L2V5.*.hdf (apriori fraction < 50%)

Satellite Measurements

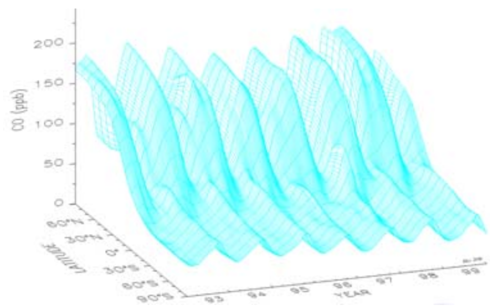
Upper Tropospheric CO



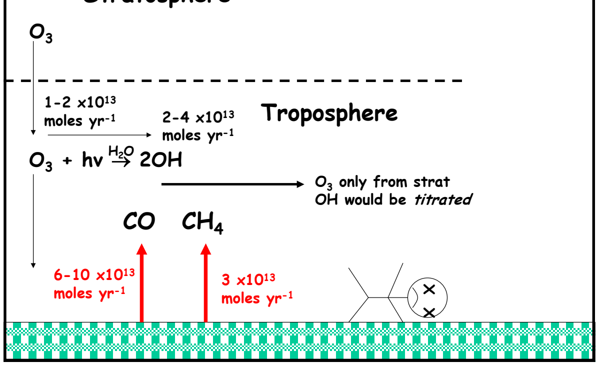
Gridded at 1x1deg from MOP02-200410??-L2V5.*.hdf (apriori fraction < 50%)

Global Distribution of CO

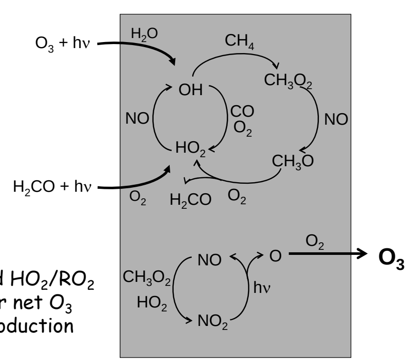
NOAA/CMDL surface air measurements



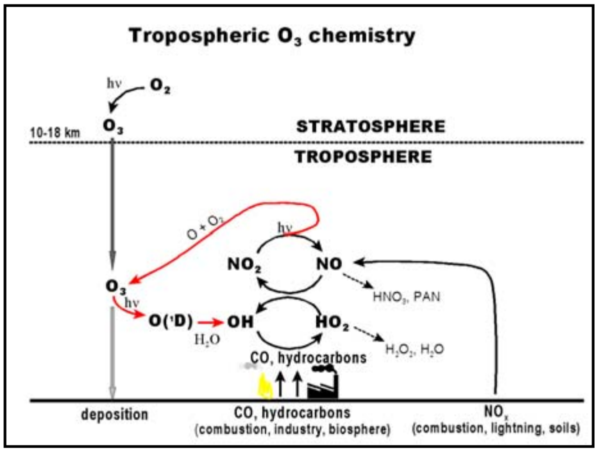
OH Titration Problem



HO_x and NO_x Catalyzed O_3 Production



Need HO_2/RO_2 for net O_3 production

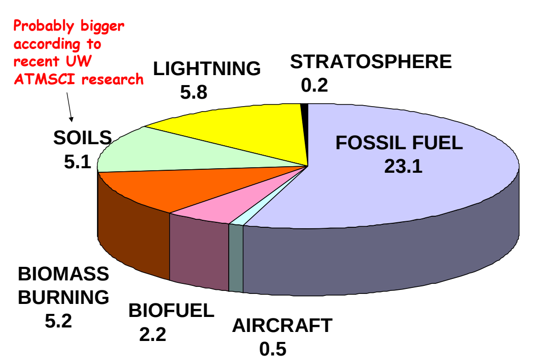


Questions

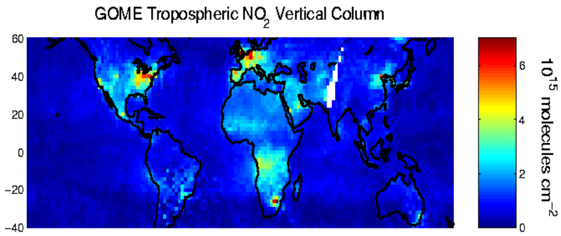
1. NO also reacts with O_3 (as in the stratosphere) to produce NO_2. In fact, the rate of conversion of NO to NO_2 is dominated by this reaction in the troposphere. What is the effect of this reaction on O_3 *production*?

2. Loss of NO_x in the troposphere takes place by $NO_2 + OH \rightarrow HNO_3$, same as in the stratosphere. What is the effect of this reaction on tropospheric ozone?

Tropospheric NO_x Sources (Tg N yr^{-1})



Tropospheric NO_2 from Space

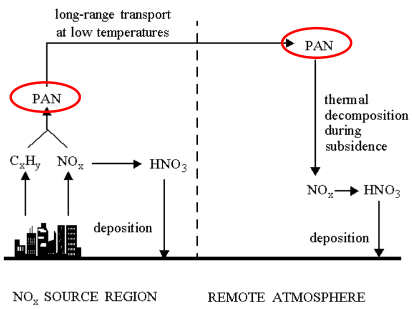


NO_x Lifetime < 1 day! Fraction transported away from source regions very low

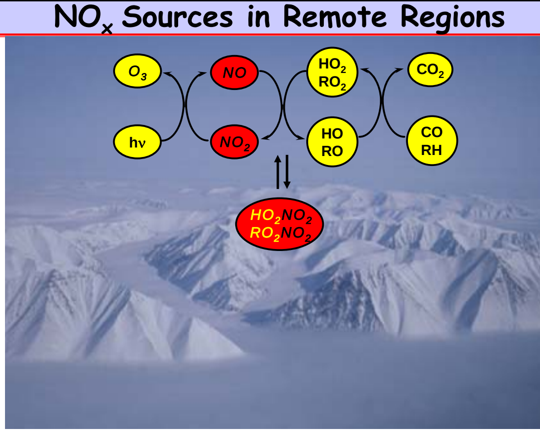
Martin et al. [2002]

Long-Range Transport of NO_x

By NO_x Reservoir: Peroxyacetyl Nitrate (PAN)



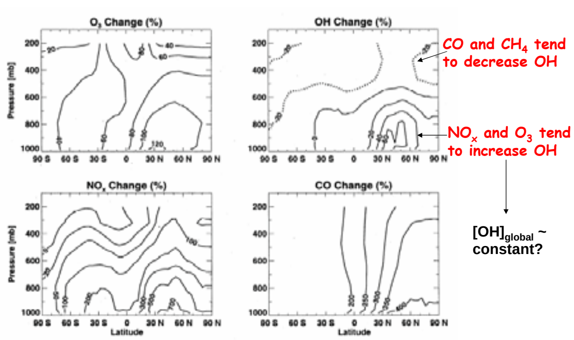
NO_x Sources in Remote Regions



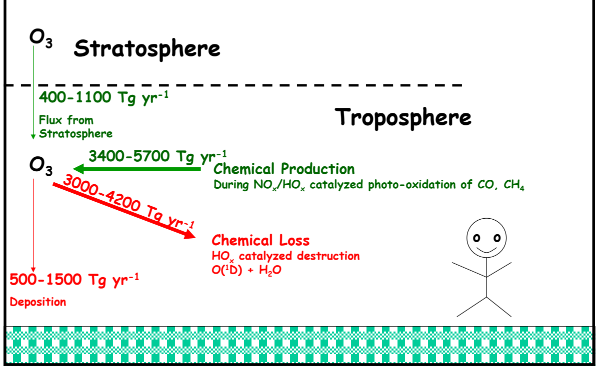
Question

- Anthropogenic activity has lead to the increase of NO_x, CO, and CH_4 emissions, with roughly factors of 2-4 increases of each over pre-industrial times. How have these changes affected OH concentrations?

Predicted Change Since Pre-Industrial Times



Global Tropospheric O_3 Budget



Tropospheric Halogen Chemistry

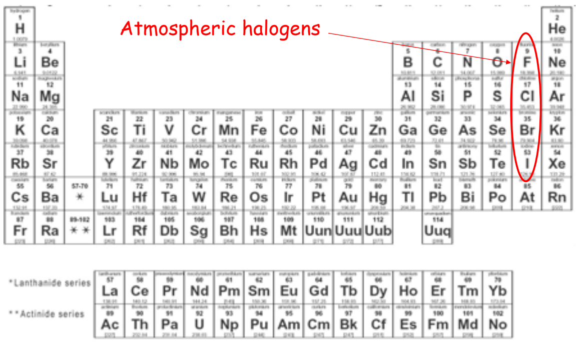
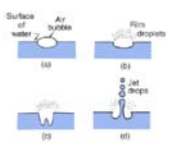


Image from:
http://www.bpc.edu/mathscience/chemistry/images/periodic_table_of_elements.jpg

Sources of Tropospheric Halogens

Sea-salt: $Cl^-_{(aq)}$, $Br^-_{(aq)}$, $I^-_{(aq)}$

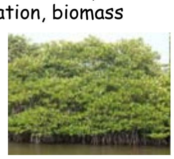


Volcanoes

Terrestrial and aquatic ecosystems, agricultural fumigation, biomass burning

Methyl chloride: CH_3Cl

Methyl bromide: CH_3Br



Other industrial activity?

Trop. Production of Reactive Halogens

"Active" (gas-phase) halogen species:

Br_2, Br, BrO, HOBr (similar for Cl and I, also BrCl)

soluble in water

Production of reactive halogens from e.g. $Br^-_{(aq)}$ and CH_3Br occurs via photochemical oxidation reactions.

Exact production mechanisms are not always well-understood.

Polar Ozone Depletion Events (ODEs)

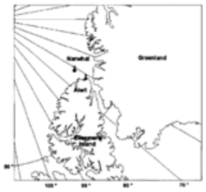
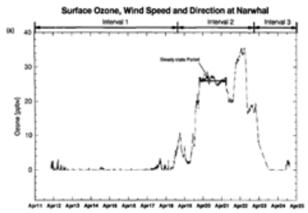


Fig. 1. The observation site, Ice Camp Narwhal, near Alert.

Low O_3 concentrations occur when wind originates from over the Arctic ocean and is anticorrelated with "filterable" bromine

Strong tropospheric O_3 depletion (< 10 ppbv) at the surface in polar regions during springtime



Gong et al., Atmospheric Environment, 1997

High BrO Associated with Spring Sea-Ice

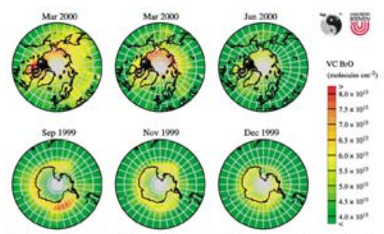


Figure 5 Monthly averages of BrO vertical columns (in molecules cm^{-2}) in winter/spring for the northern hemisphere (upper row) and the southern hemisphere (lower row) (courtesy Andreas Richter).

vonGlasow and Crutzen, 2003

Main source of BrO above is from photochemical reactions on top of fresh (one-year old) sea-ice, where halides get concentrated on the surface upon freezing.

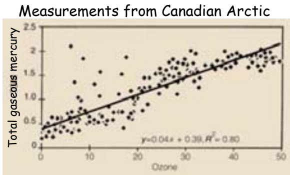
Mercury Depletion Events

Oxidation by halogens

$Hg^0_{(g)} \rightarrow Hg(II)_{(particulate)}$

Deposition to surface

Measurements from Canadian Arctic



Schroeder et al., 1998

Implications for health of humans and Arctic ecosystems following flushing of Hg(II) in meltwater during spring and summer

Oxidation of Alkanes

High reactivity of Cl with hydrocarbons

$CH_4 + Cl \rightarrow HCl + CH_3$

Halogens may influence the oxidation capacity of the atmosphere through their impacts on oxidant concentrations (e.g. O_3) and as direct oxidants them selves (e.g. reducing the lifetime of CH_4).

Understanding of halogen chemistry and their role in the chemical budgets of other trace gases in the atmosphere is only beginning to emerge, and is an active area of research!