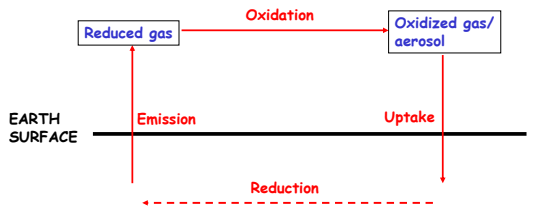
Tropospheric Chemistry

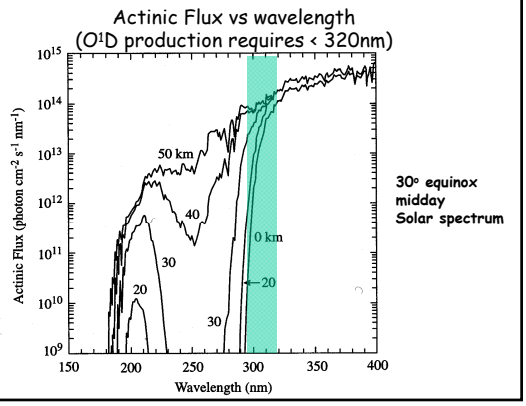
READING: Chapter 11 of text

- 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

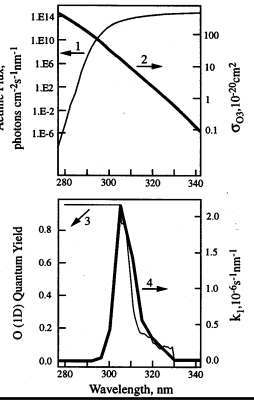


O(^{1}D) Production in Troposphere?

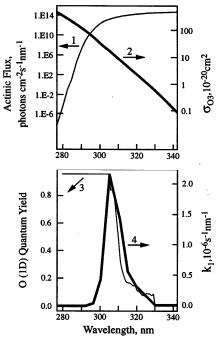


$O(^1D)$ production in the Troposphere?

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



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*

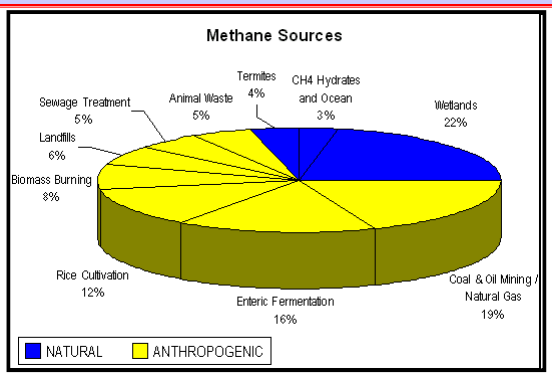
$HCFC + OH \rightarrow H_2O + \ldots$

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 to for geo-engineering affect the tropospheric OH source?
3. How might global warming affect the source rate of OH in the troposphere?

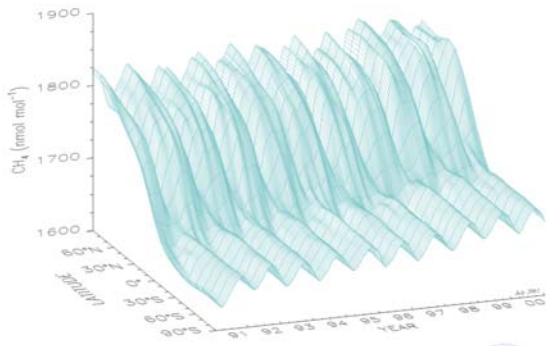
Global Sources of Methane



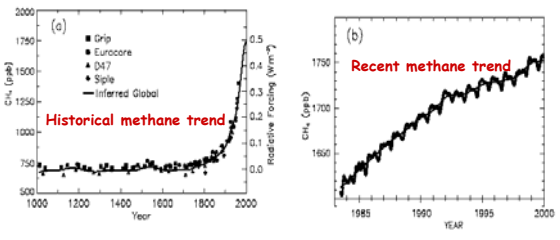
Augenbraun, et al, NASA GISS 1997 Global Methane Inventory.

Global Distribution of Methane

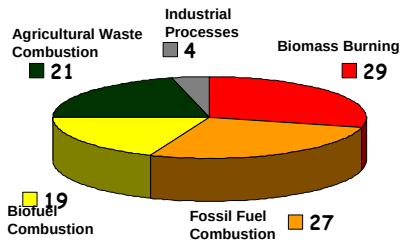
NOAA/CMDL surface air measurements



Historical Trends In Methane



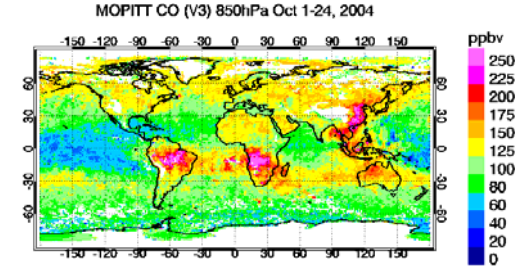
Global Sources of CO



Based on Olivier, et al *Chemosphere* 1999

Satellite Measurements

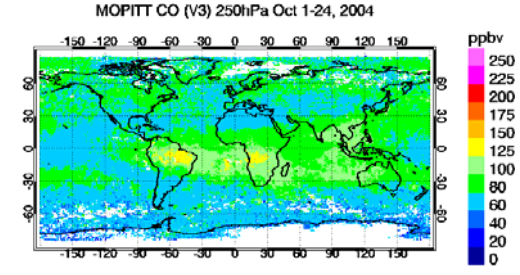
Lower Tropospheric CO



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

Satellite Measurements

Upper Tropospheric CO



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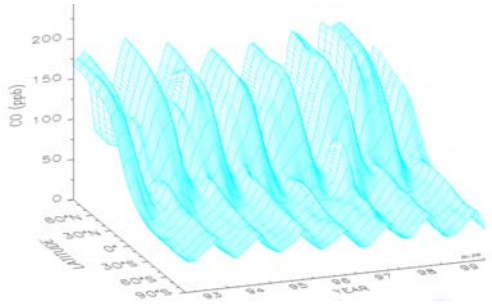
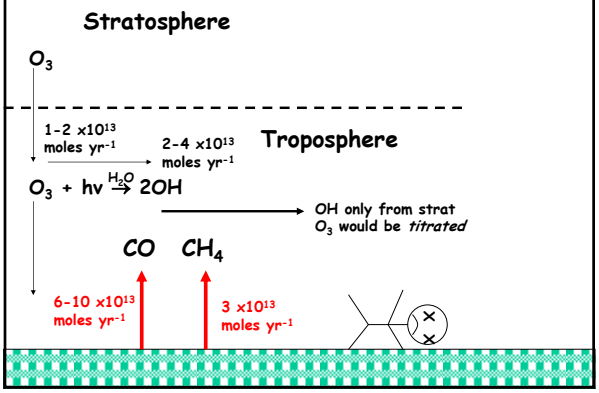
Global Distribution of CO

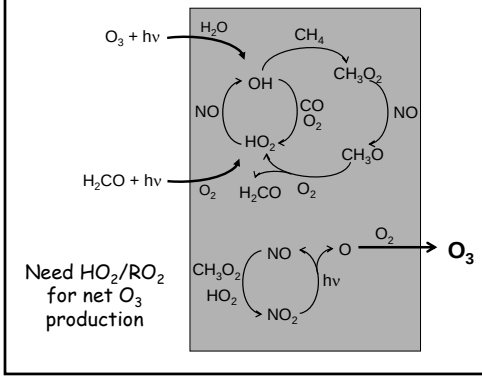
NOAA/CMDL surface air measurements



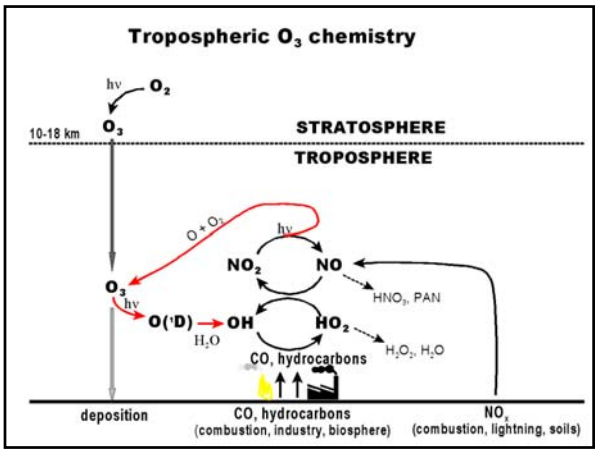
OH Titration Problem



HO_x and NO_x Catalyzed O_3 Production



Need HO_2/RO_2 for net O_3 production

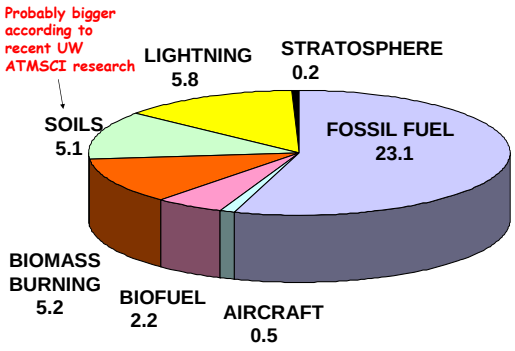


Questions

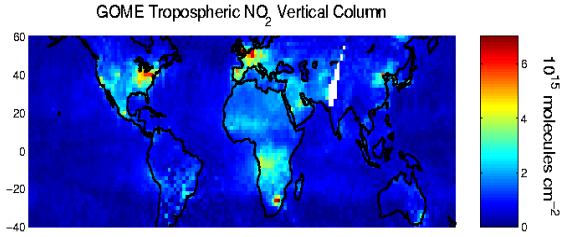
1. NO also reacts with O_3 (as in the stratosphere) to produce NO_2. In fact, the rate of conversion of NO to NO_2 is dominated by this reaction in the troposphere. What is the effect of this reaction on O_3 *production*?

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

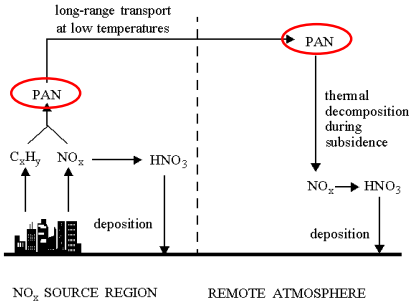


NO_x Lifetime < 1 day! Fraction transported away from source regions very low

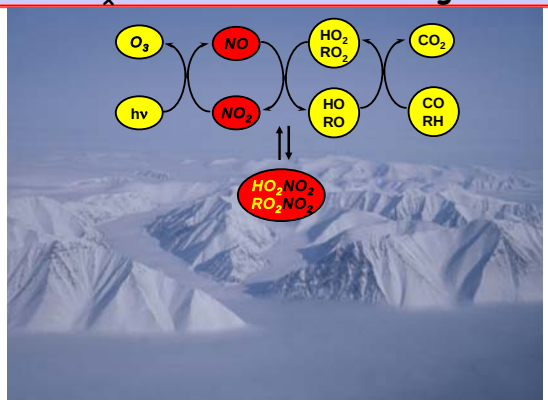
Martin et al. [2002]

Long-Range Transport of NO_x

By NO_x Reservoir: Peroxyacetyl Nitrate (PAN)



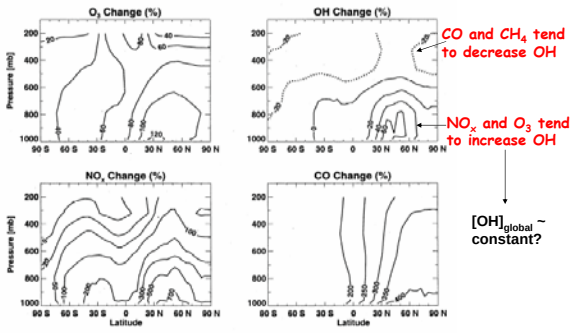
NO_x Sources in Remote Regions



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



CO and CH_4 tend to decrease OH

NO_x and O_3 tend to increase OH

$[OH]_{global}$ ~ constant?

Global Tropospheric O_3 Budget