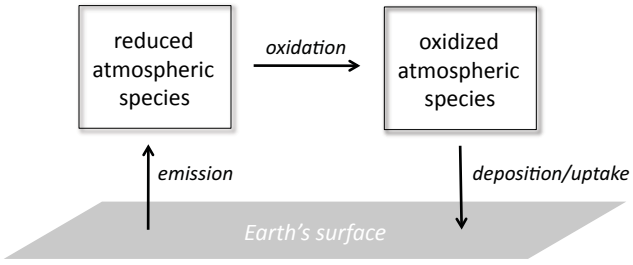
Atmos. Chem. Lecture 10, 10/9/13: Tropospheric Chemistry 1

- Troposphere: intro/background
- Sources, cycling of HO_x
- Sources, cycling of NO_x
- Carbon monoxide oxidation

The troposphere



[Note: Additional material is discussed here during lecture.]

Early tropospheric chemistry research: LA Smog

Haagen-Smit, *Ind. Eng. Chem.* 44:1342 (1952): Smog from photochemical oxidation of hydrocarbons in the presence of NO_x; description of ozone, aerosol pollution:

> *"Photochemical and other reactions change normally harmless compounds into objectionable ones. On the other hand, substances irritating when released may soon be converted into harmless ones. A proper evaluation of the contribution of air pollutants to the smog nuisance must include not only the time and place of their emission, but also their fate in the air."*

Haagen-Smit et al., *Ind. Eng. Chem.* 45:2086 (1953): ozone from HCs and NO_x

> *"The release of large quantities of hydrocarbons to the air and the simultaneous presence of nitrogen oxides from combustion processes explains the relatively high ozone content"*

First laboratory simulations of tropospheric chemistry

"To study those reactions further a fumigation room was built from Plexiglas…"

TABLE I. EYE IRRITATION OBSERVED IN THE OXIDATION OF OLEFINS

(With 0.4 p.p.m. of nitrogen dioxide and 0.2 p.p.m. of ozone under influence of sunlight)

Olefin	Hydrocarbon Concentration, P.P.M.	Degree of Eye Irritation
Ethylene	1	Doubtful
Propene	1	None
1-Butene	3	Severe smog
1-Butene	0.5	Severe smog
1-Butene	0.2	Light smog
2-Butene	3	Medium smog
2-Butene	1	Medium smog
2-Butene	0.5	Medium smog
Isobutene	1	None
1-Hexene	1	Medium smog

Haagen-Smit 1952

Early tropospheric chemistry research

Cadle and Allen, *Science* 167:3916 (1970): Troposphere is relatively inert(!); only photolysis or reactions with O or O_2 matter

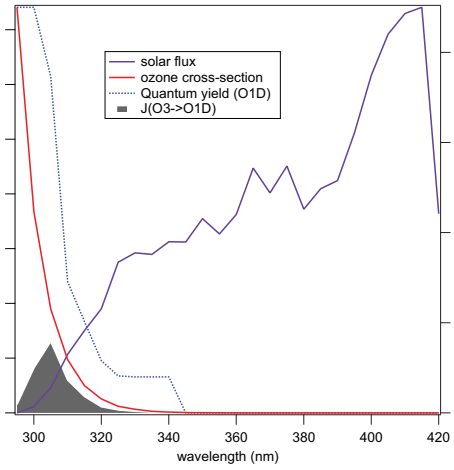
"*The chemistry of the troposphere is mainly that of a large number of atmospheric constituents and of their reactions with molecular oxygen*"

Robbins and Robbins, "Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants", *SRI report*, 1967: Lifetime of CO estimated at 2.7 years (loss by soil)

Weinstock, *Scienc* 166:224 (1969): ^{14}CO measurements → lifetime of 0.1 years, loss by OH

Levy, *Scienc* 173:141 (1971): OH generated from ozone photolysis

Ozone photochemistry



Courtesy of James Hunter. Used with permission.

courtesy J. Hunter

Atmospheric OH

$O_3 + h\nu \rightarrow O(^3P) + O_2$

$\rightarrow O(^1D) + O_2$

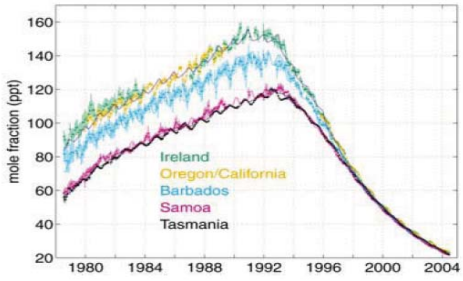
$O(^1D) + M \rightarrow O(^3P) + M$

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

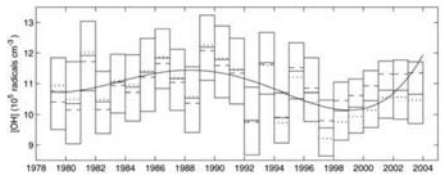
[Note: Additional material is discussed here during lecture.]

Measuring OH: Tracers

CCH_3CCl_3

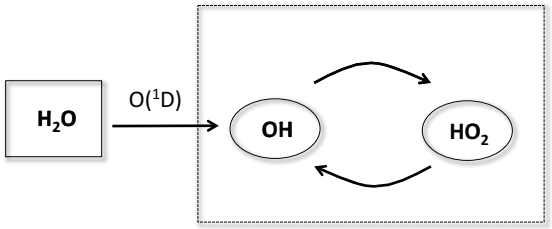


OH



Prinn et al, *GRL* 32, L07809 (2005)

HO_x cycle: Troposphere



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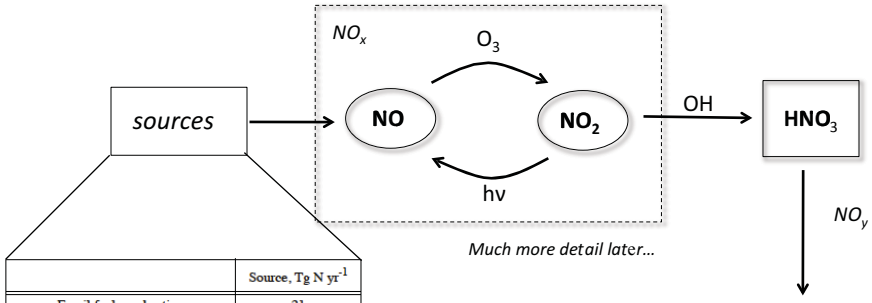
Simple NO_x cycle: Troposphere

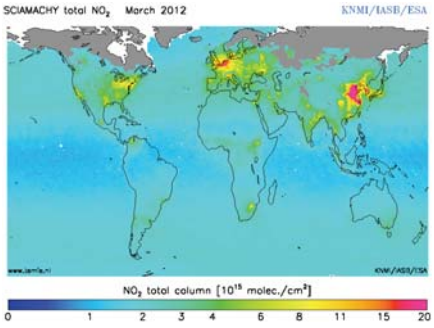


	Source, Tg N yr^{-1}
Fossil fuel combustion	21
Biomass burning	12
Soils	6
Lightning	3
NH_3 oxidation	3
Aireraft	0.5
Transport from stratosphere	0.1

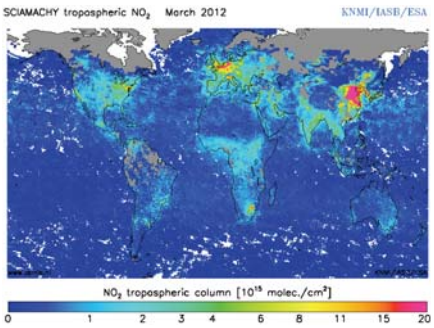
Jacob

Global NO_2

total column



tropospheric column



From SCIAMACHY (**SC**anning **I**maging **A**bsorption spectro**M**eter for **A**tmospheric **C**artograp**HY)**

March 2012

http://www.temis.nl/airpollution/no2.html

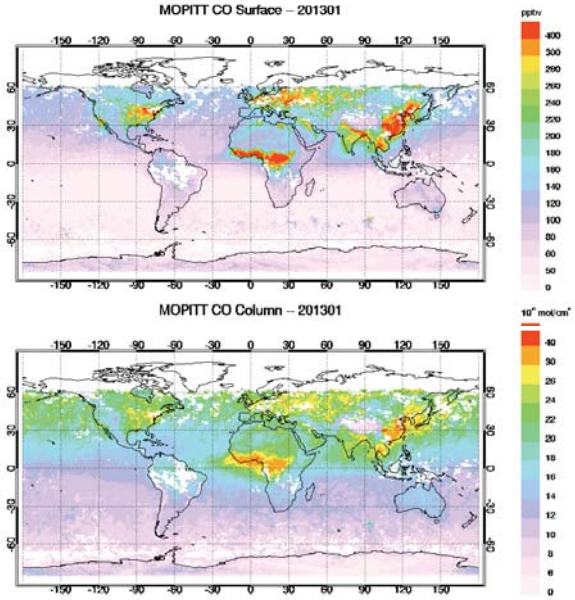
Carbon monoxide: Sources, sinks

Image removed due to copyright restrictions. See Table 11-1 in Jacob, Daniel. *Introduction to Atmospheric Chemistry*. Princeton University Press, 1999.

[Note: Additional material is discussed here during lecture.]

Jacob

Global carbon monoxide



MOPITT
(**M**easurements
Of **P**ollution **I**n
The **T**roposphere)
(Jan 2013)

http://www.acd.ucar.edu/mopitt/MOPITT/data/plots6j/maps_mon.html

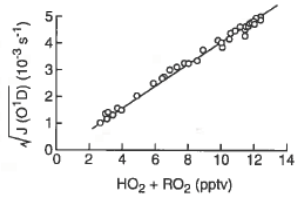
$CO + HO_x + NO_x + h\nu$

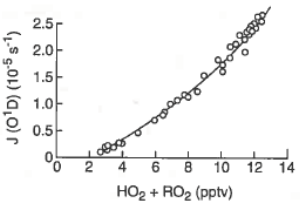
$CO + OH\ (+O_2) \rightarrow HO_2 + CO_2$

[Note: Additional material is discussed here during lecture.]

dependence of $[HO_2]$ on P_{HOx}

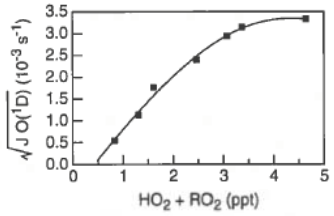
Remote: Cape Grim, Tasmania

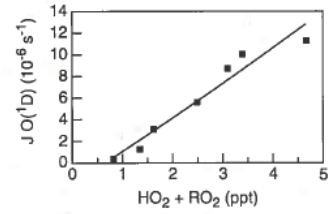




Penkett et al. , JGR 102: 12805 (1997)

Polluted: Mace Head, Ireland





Carpenter et al. , JGR 102: 25417 (1997)

FP&P

1.84J / 10.817J / 12.807J Atmospheric Chemistry
Fall 2013