Oxidizing Power of the Troposphere

Oxidation in Earth's atmosphere compared to Venus and Mars

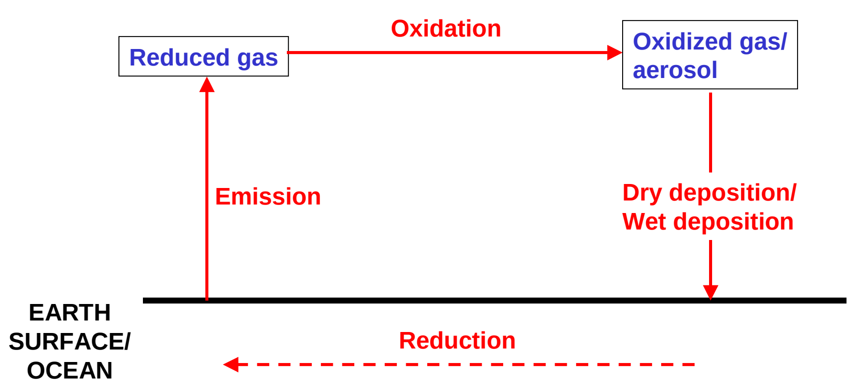
Chemical Atmospheric Composition (in percent)

	VENUS	EARTH	MARS
N_2	3.4	78.08	2.7
O_2	0.007	20.9	0.13
Ar	0.007	0.93	1.6
CO_2	96	0.03	95.3
H_2O	0.1-0.5	2	0.03

Chemistry of the Natural Atmosphere, P. Warneck, chap 12, 1987

Oxidation in the Earth's troposphere

- Due to abundance of O_2, Earth's atmosphere is oxidizing (e.g., $SO_2 \rightarrow SO_4^{2-}$; $CH_4 \rightarrow CO$; $CO \rightarrow CO_2$; $NO_2 \rightarrow HNO_3$)
- After O_2, O_3 is most abundant oxidant
- But direct oxidation of non-radical species by reaction with O_2 and O_3 is too slow to be of consequence (large bond energies $\rightarrow$ O_2 and O_3 largely unreactive)
- The OH radical is the most important oxidant in the troposphere
- Other atmospheric oxidants include NO_3, halogen radicals, and H_2O_2 (in the aqueous-phase)



Importance of the hydroxyl radical - OH

Air Pollution and Tropospheric Ozone

Lifetime of many trace gases important for local and regional air quality. Formation of ozone.

Stratospheric Ozone

Oxidation of HCFCs, methyl halides, and methane. Catalytic ozone loss.

OH CHEMISTRY

Aerosols

Oxidation of SO_2, DMS, NO_2: aerosol formation and composition.

Climate Change

Control of radiatively active species including methane, HCFCs, ozone, and aerosols.

Atmospheric lifetimes of selected species

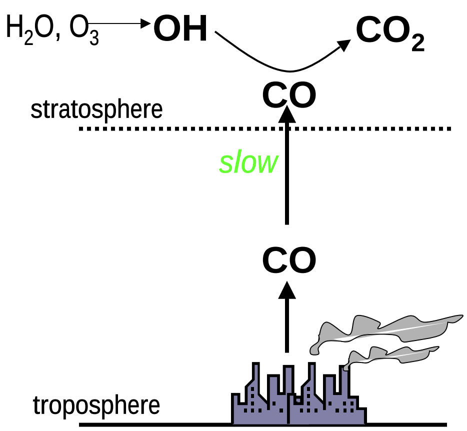
Species	Lifetime[a]	Reference	
CH_3CCl_3	4.8 y *(5.7 y)*	WMO [1999]	(solvant)
CH_4	8.4 y *(8.9 y)*	*ibid.*	
CHF_2Cl	11.8 y *(12.3 y)*	*ibid.*	(HCFC 22, refrigerant)
CH_3Br	0.7 y *(1.7 y)*	*ibid.*	
Isoprene[b]	~ 1 h *(~ 1 h)*	Jacob et al. [1989]	(C_5H_8, emitted by vegetation)
CO	2 mo *(2 mo)*	Logan et al. [1981]	
NO_x ($NO+NO_2$)	~ 1 d *(~1 d)*[c]	Dentener and Crutzen [1993]	
SO_2	~ 1 d *(2 wks)*[d]	Chin et al. [1996]	
$(CH_3)_2S$	~ 1 d *(~1 d)*	*ibid.*	

The first number given for each entry in the column is the mean atmospheric lifetime, and the second number in parentheses is the mean atmospheric lifetime against oxidation by OH.

Jacob, The oxidizing power of the atmosphere, Handbook of Weather, Climate and Water, 2000.

View prior to 1970s: Inert troposphere

(only source of oxidants in the stratosphere)



With an inert troposphere:
Only sink of CO would be in the stratosphere → implies long lifetime for CO (~10 years), limited by transport rate of air into the stratosphere
→With increasing emissions from fossil fuel combustion will CO accumulate in the troposphere?

View of an inert troposphere challenged [Weinstock, 1969]:
^{14}CO measurements in troposphere imply a 2-month lifetime for CO → there MUST be a tropospheric sink!

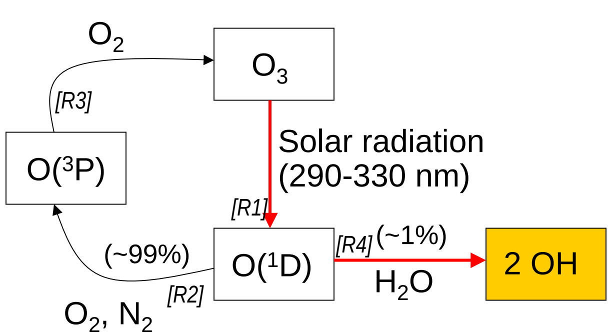
Primary source of tropospheric OH [Levy, 1971]

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $\lambda<330$ nm   [R1]

$O(^1D) + M \rightarrow O(^3P) + M$ [R2]

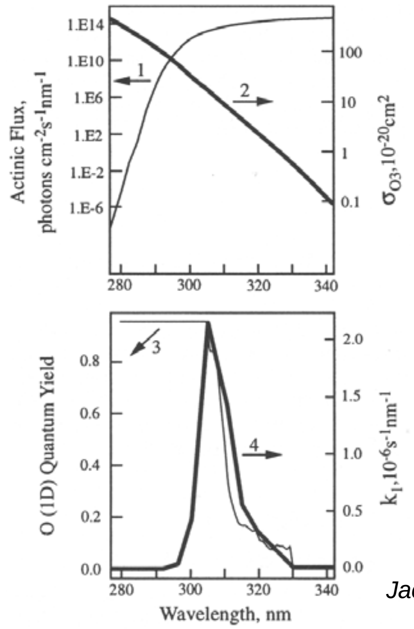
$O(^3P) + O_2 + M \rightarrow O_3 + M$ [R3]

$O(^1D) + H_2O \rightarrow OH + OH$ [R4]



$$P_{OH} = 2k_4[O(^1D)][H_2O] = 2k_1k_4[O_3][H_2O]/(k_2[M])$$

Dependence of O_3 photolysis rate constant on wavelength



Photolysis of O_3 to $O(^1D)$ determined by a narrow band of radiation: 290-330 nm ← combined wavelength dependences of actinic flux (q), O_3 absorption cross section (σ), and $O(^1D)$ quantum yield (ϕ).

$$J(O_3 \rightarrow O(^1D)) = \int_\lambda q\, \sigma\, \phi\, d\lambda$$

→Radiation in 290-330 nm wavelength range Is strongly absorbed by overhead O_3 , and $O(^1D)$ production thus very sensitive to stratospheric O_3 layer

Jacob, Introduction to Atmospheric Chemistry, 1999

Sinks of OH

Reaction of OH with OH and CH_4 are the dominant sinks of OH in the troposphere:

$$CO + OH \rightarrow CO_2 + H$$
$$CH_4 + OH \rightarrow CH_3 + H_2O$$

In the lower troposphere over continents, reaction with non-methane hydrocarbons (NMHCs) is also important:

$$NMHC + OH \rightarrow products$$

Lifetime of OH ~ 1 second!

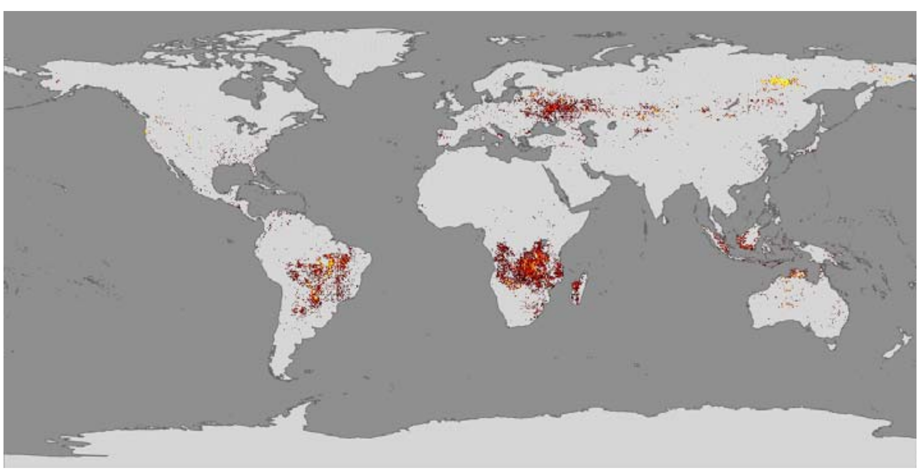
Budget of carbon monoxide

Table 11-1 Present-Day Global Budget of CO

	Range of estimates (Tg CO yr $^{-1}$)
Sources	1800–2700
➡ Fossil fuel combustion/industry	300–550
➡ Biomass burning	300–700
Vegetation	60–160
Oceans	20–200
➡ Oxidation of methane	400–1000
➡ Oxidation of other hydrocarbons	200–600
Sinks	2100–3000
Tropospheric oxidation by OH	1400–2600
Stratosphere	~ 100
Soil uptake	250–640

Contribution from anthropogenic sources ~ 85%

Global fires observed by the MODIS satellite: 2001-2002

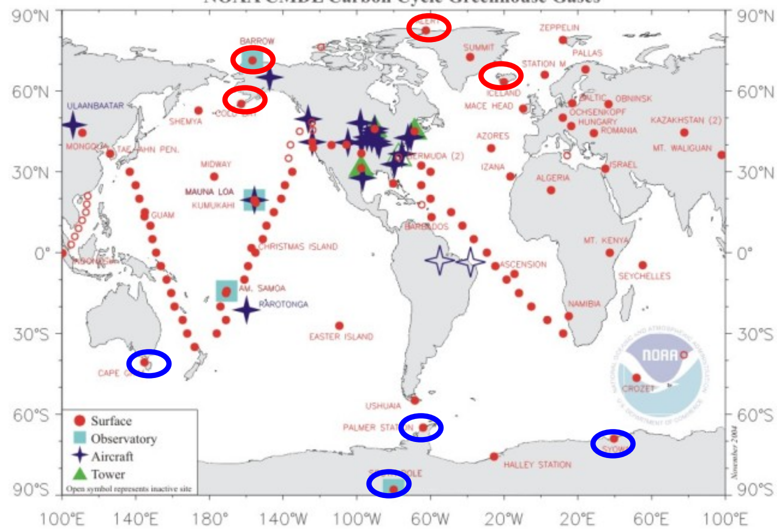


http://earthobservatory.nasa.gov/Newsroom/NewImages/images.php3?img_id=10304

Quicktime movie: fire_640.mov

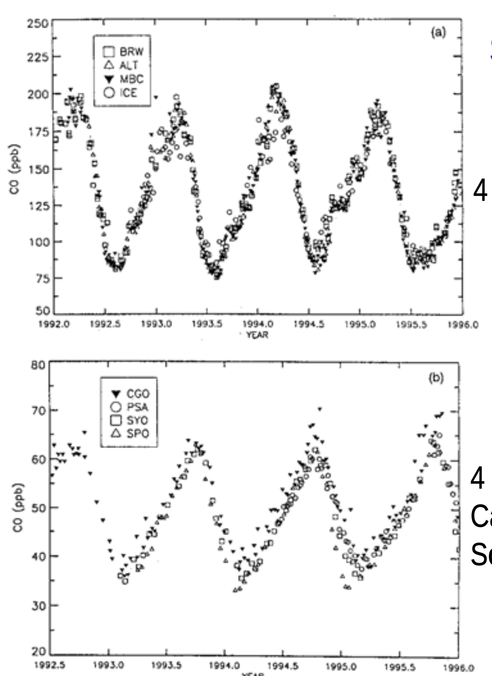
Measurement Programs

NOAA CMDL Carbon Cycle Greenhouse Gases



The NOAA CMDL Carbon Cycle Greenhouse Gases group operates 4 measurement programs. In situ measurements are made at the CMDL baseline observatories: Barrow, Alaska; Mauna Loa, Hawaii; Tutuila, American Samoa; and South Pole, Antarctica. The cooperative air sampling network includes samples from fixed sites and commercial ships. Measurements from tall towers and aircraft began in 1992. Presently, atmospheric carbon dioxide, methane, carbon monoxide, hydrogen, nitrous oxide, sulfur hexafluoride, and the stable isotopes of carbon dioxide and methane are measured. Group Chief: Dr. Pieter Tans, Carbon Cycle Greenhouse Gases, Boulder, Colorado, (303) 497-6678 (pieter.tans@noaa.gov, http://www.cmdl.noaa.gov/ccgg).

Surface observations of CO



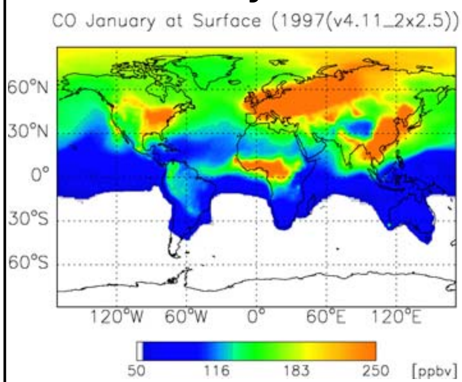
4 sites in high Northern Hemisphere
Barrow, Alert, Mould Bay, Iceland

4 sites in high Southern Hemisphere
Cape Grim, Palmer Station, Syowa, South Pole

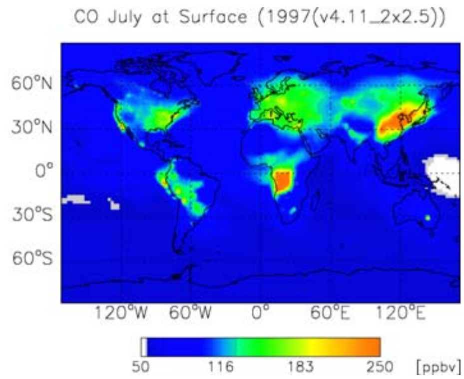
Novelli et al., JGR, 103, 19015, 1998.

Model-calculated surface CO concentrations: GEOS-Chem global model of tropospheric chemistry

January: surface



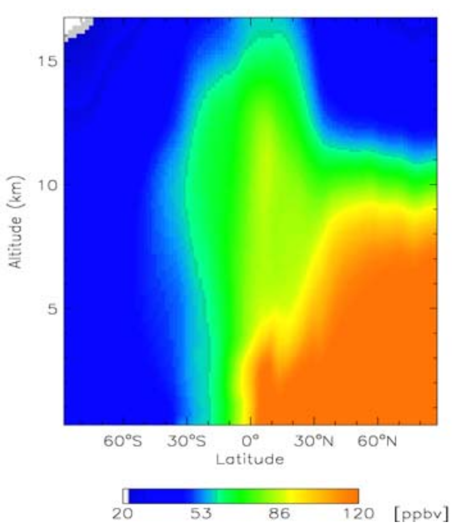
July: surface



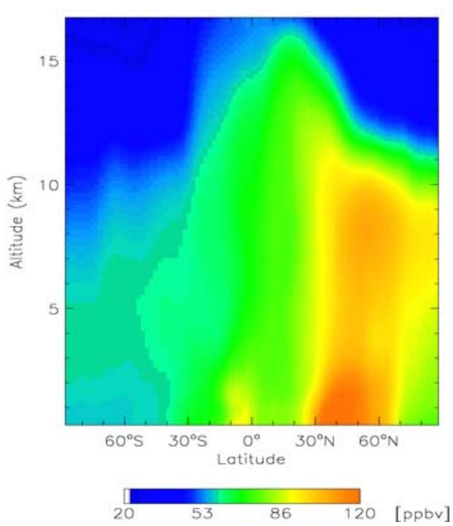
Generate your own plots at:
http://www.atmos.washington.edu/~jaegle/geoso3_start.html

CO Zonal average

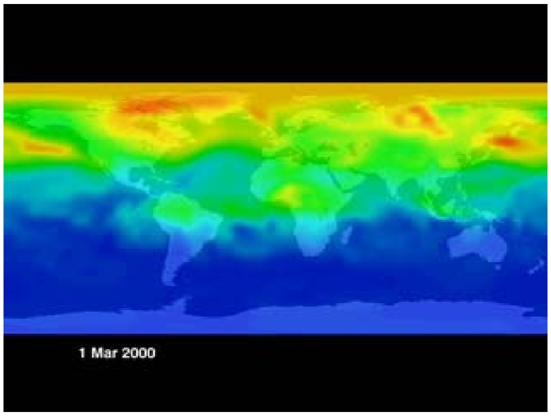
January



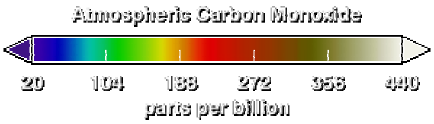
July



Animation of CO at 500 mbar – combination of global model and satellite observations Mar-Dec 2000

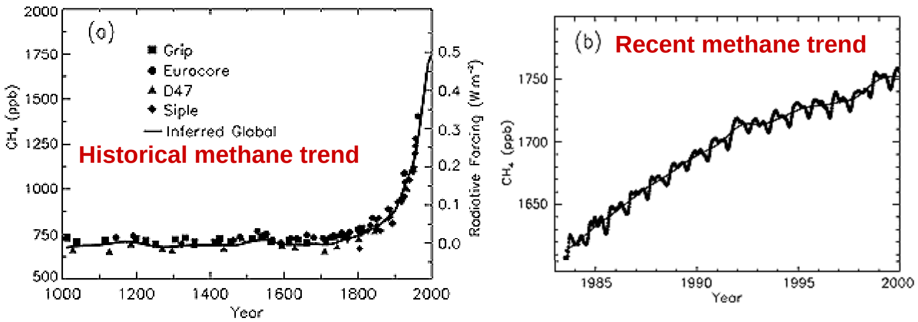


TERRA: MOPITT instrument



Human influence on Methane

Increase from 700 ppbv → 1745 ppbv



…decreasing rate of increase?

IPCC, 2001

Biological formation of methane

- Anaerobic decomposition of organic material by methanogenic bacteria (flooded soils, wetlands, landfills, digestive tracts..)

$CH_2O \rightarrow ½\ CH_4 + ½\ CO_2$

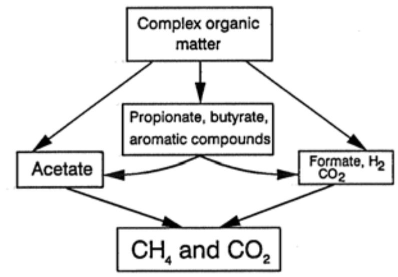
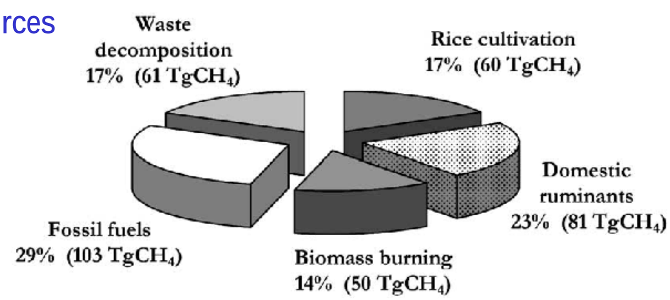


Fig. 1. Organic matter decomposition in methanogenic ecosystems

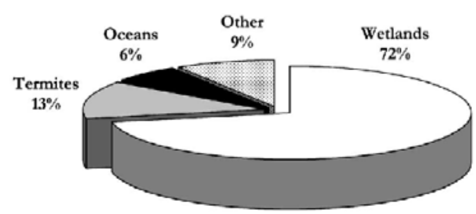
- Methane production is temperature dependent, with maximum growth 37°-45°C

Anthropogenic sources of methane: ~355 Tg CH_4/year

~ 70% of total sources



Natural sources of methane: ~150 Tg CH_4/year



Increase in cattle and rice cultivation

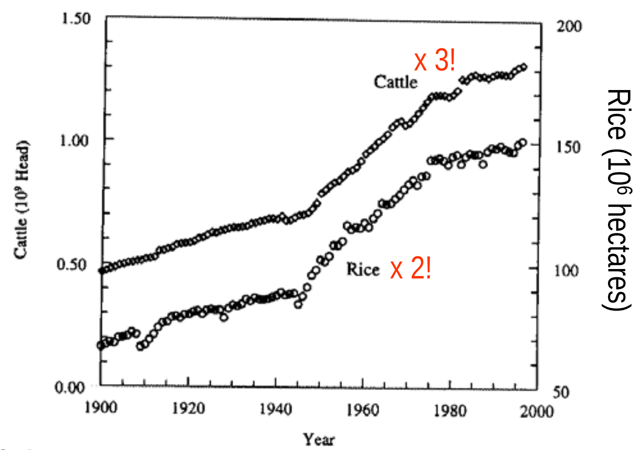


Fig. 2. Increases in cattle populations and area of rice harvested for the turn of the centur tohe present. Cattle populations have increased by a factor of almost 3 and rice fields by during this time. These agricultural sources represent a large role of human activities on th global methane cycle.

"Atmospheric methane: Its role in the global environment" Khalil (ed.) 2000

Methane lifetime

–Loss of methane by atmospheric oxidation:

CH_4 + OH → CH_3 + H_2O → … CO + products..→ CO_2 + products
~ 8 year lifetime

– The reaction CH_4 + OH represents ~30% of OH loss

– Increase in CH_4 emissions → increase in CH_4 concentrations → decrease in OH levels → increase in the lifetime of CH_4 → further increases in CH_4 concentrations (positive feedback)

– Example: 1% increase in CH_4 results in a 0.32% decrease in OH → effective CH_4 lifetime ~ 12 years