1.84/10.817/12.807: Atmospheric Chemistry

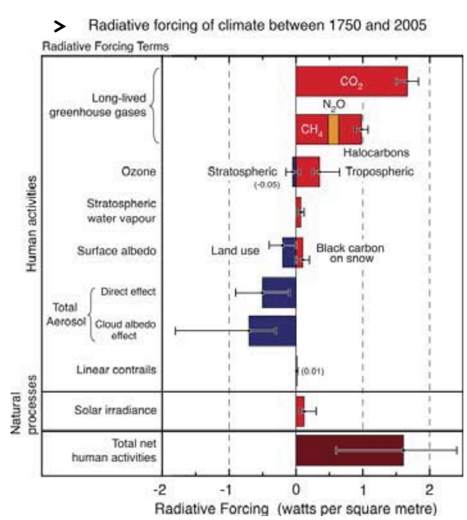
Prof. Jesse Kroll

Today:

1) Motivation/Introduction
2) Course overview/outline
3) Atmosphere, chemistry basics

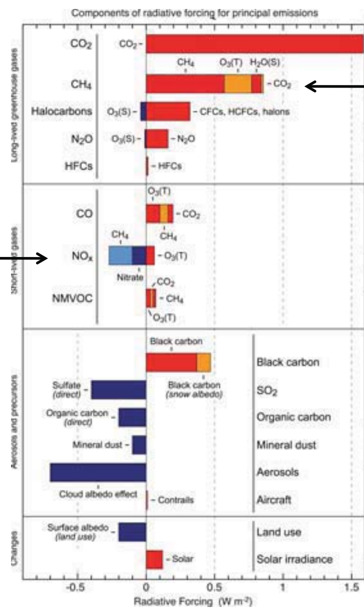
Climate and chemistry

Change in net irradiance (incoming minus outgoing radiation) since 1750



IPCC 2007: P. Forster et al., *Changes in Atmospheric Constituents and in Radiative Forcing, Cambridge, United Kingdom and New York, NY, USA:* Cambridge University Press, 2007

Climate and chemistry



Methane oxidation forms water ($CH_4 + OH \rightarrow CH_3 + H_2O$) and eventually CO_2; under polluted (high NO_x) conditions, forms ozone as well

Nitrogen oxides form ozone (warming), which in turn increases oxidation rates (more OH), decreasing CH_4 (cooling); also forms nitrate aerosol (cooling)

IPCC 2007: P. Forster et al., *Changes in Atmospheric Constituents and in Radiative Forcing, Cambridge, United Kingdom and New York, NY, USA:* Cambridge University Press, 2007

Ozone depletion

Nature Vol. 249 June 28 1974

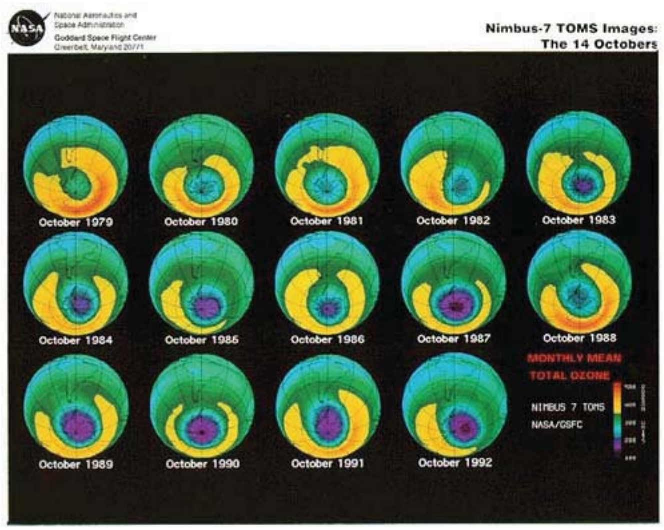
Stratospheric sink for chlorofluoromethanes : chlorine atomc-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

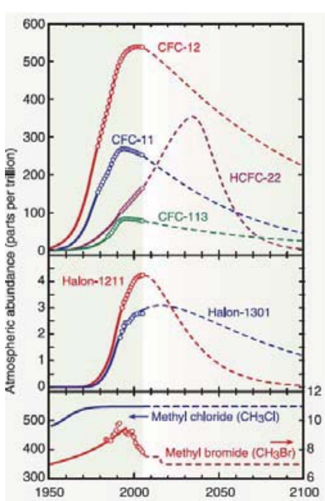
Ozone depletion



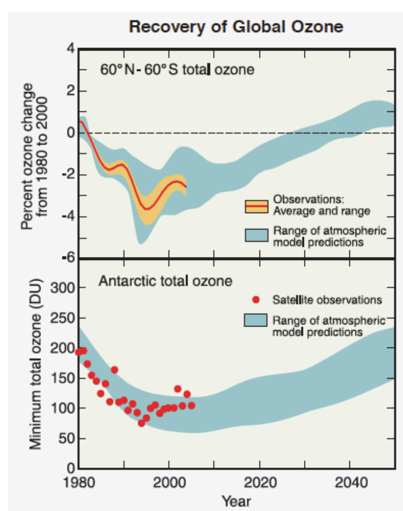
This image is in the public domain.

TOMS (Total Ozone Monitoring Satellite) Data
(global depletion occurring as well)

Ozone depletion: Montreal Protocol



This image is in the public domain.



This image is in the public domain.

WMO/UNEP, *Scientific Assessment of Ozone Depletion: 2006*

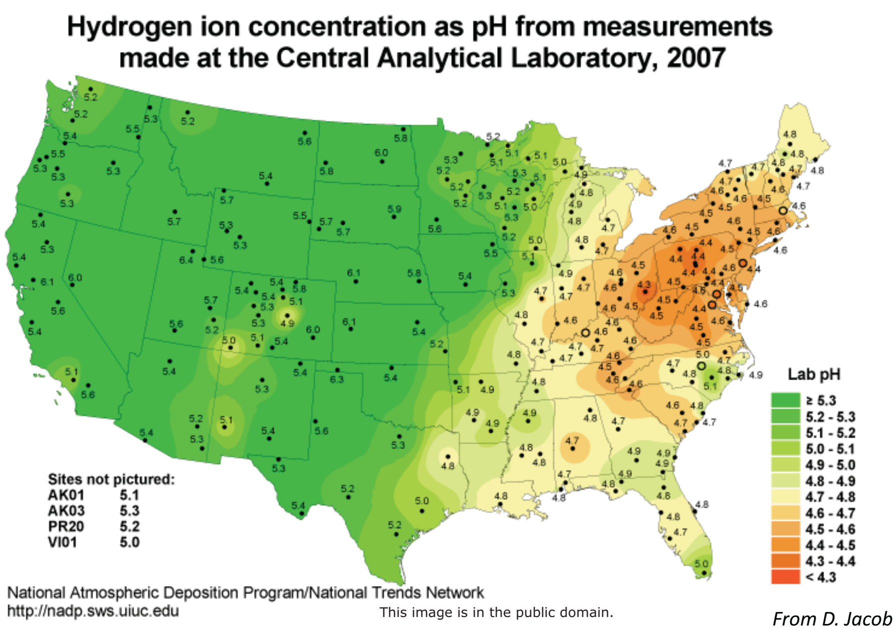
Ecological health/biogeochemistry

acid deposition

nutrient deposition

wikipedia

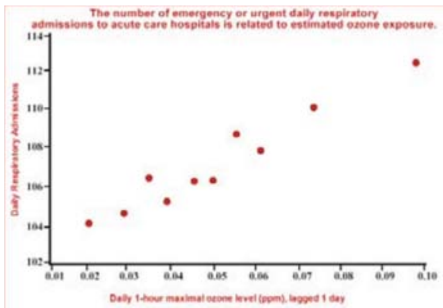
Acid rain



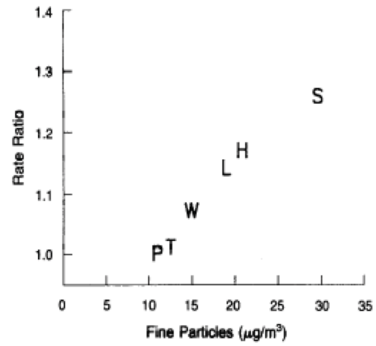
From D. Jacob

Human health

Ozone



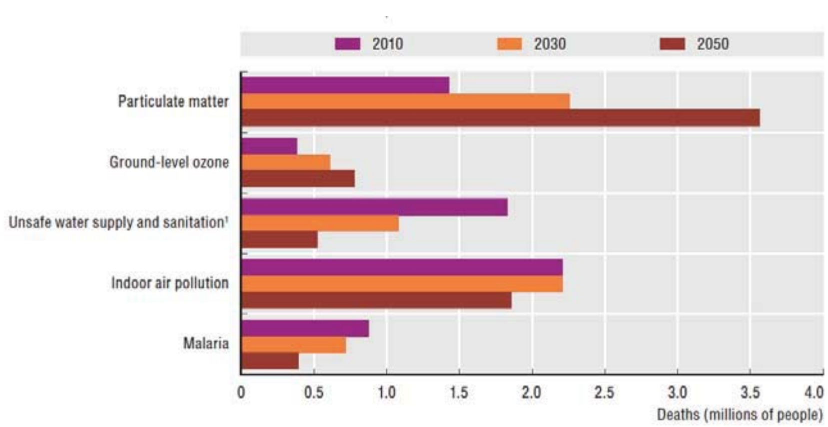
Particulate matter



http://www.epa.gov/o3healthtraining/population.html

D. W. Dockery et al., *N. Engl. J. Med.* 329, 1753-1759 (1993)

Air pollution and health, 2010-2050



OECD Environmental Outlook to 2050

Visibility

WHO Guideline: 50 μg/m^3
averaged over 24 hrs

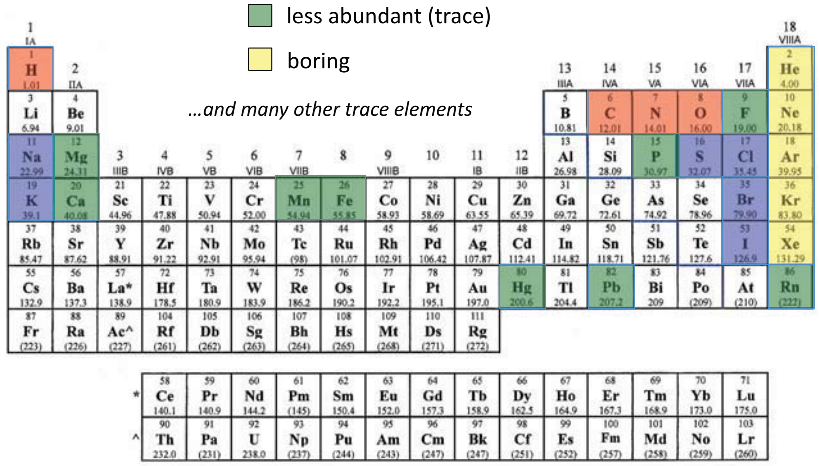
Images removed removed due to copyright restrictions.

http://news.bbc.co.uk/2/hi/in_pictures/7506925.stm

Key elements in the atmosphere

- abundant
- also important
- less abundant (trace)
- boring

…and many other trace elements



Chemical composition of atmosphere

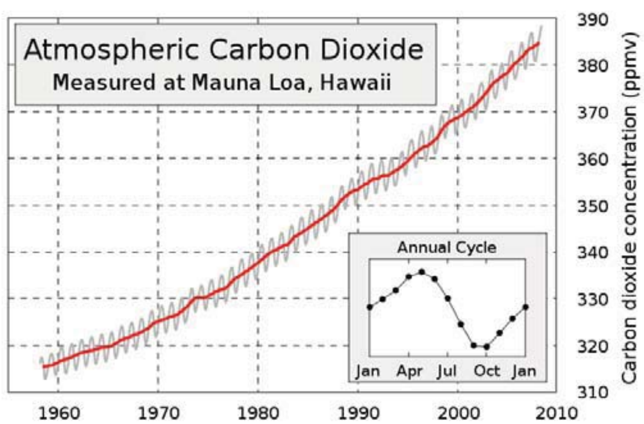
Increasing due to human activity

Chemical Species	*Volume fraction, ppm*
Nitrogen (N_2)	780,840 (78.084%)
Oxygen (O_2)	209,460 (20.946%)
Argon (Ar)	9,340 (0.9340%)
→ Carbon dioxide (CO_2)	390 (0.039%)
Neon (Ne)	1 .18 (0.001818%)
Helium (He)	5.24 (0.000524%)
→ Methane (CH_4)	1.79 (0.000179%)
Krypton (Kr)	1.14 (0.000114%)
Hydrogen (H_2)	0.55 (0.000055%)
→ Nitrous oxide (N_2O)	0.3 (0.00003%)
→ Carbon monoxide (CO)	0.1 (0.00001%)
Xenon (Xe)	0.09 (0.000009%)
→ Ozone (O_3)	0.0 to 0.07 (0 to 0.000007%)
→ Nitrogen dioxide (NO_2)	0.02 (0.000002%)

Not included in above dry atmosphere:

Water vapor (H_2O)	~0.40% over full atmosphere, typically 1%-4% at surface

Atmospheric CO_2



http://en.wikipedia.org/wiki/Keeling_curve

pre-industrial: ~280 ppm

Chemical composition of atmosphere

Chemical Species	*Volume fraction, ppm*
Nitrogen (N_2)	780,840 (78.084%)
Oxygen (O_2)	209,460 (20.946%)
Argon (Ar)	9,340 (0.9340%)
Carbon dioxide (CO_2)	390 (0.039%)
Neon (Ne)	18.18 (0.001818%)
Helium (He)	5.24 (0.000524%)
Methane (CH_4)	1.79 (0.000179%)
Krypton (Kr)	1.14 (0.000114%)
Hydrogen (H_2)	0.55 (0.000055%)
Nitrous oxide (N_2O)	0.3 (0.00003%)
Carbon monoxide (CO)	0.1 (0.00001%)
Xenon (Xe)	0.09 (0.000009%)
Ozone (O_3)	0.0 to 0.07 (0 to 0.000007%)
Nitrogen dioxide (NO_2)	0.02 (0.000002%)

Not included in above dry atmosphere:
Water vapor (H_2O) ~0.40% over full atmosphere, typically 1%-4% at surface

Notes on units:

1) ppm, ppb, ppt refer to volume (ppmv, ppbv, etc.)

2) For an ideal gas, **PV=nRT**, so *volume fraction* and *mole fraction* are the same

3) These are *mixing ratios*, relating amount of the compound to the total amount of air.

4) This is different from *concentration*, which is moles (or molecules) of compound per absolute volume (usually molecules/cm^3).

5) Can convert between the two, but the conversion depends on P, T (altitude)!

"Standard" conditions for temperature and pressure

Temperature	Absolute pressure	Relative humidity	Publishing or establishing entity
°C	kPa	% RH	
0	100.000		IUPAC (present definition)[1]
0	101.325		IUPAC (former definition)[1], NIST[6], ISO 10780[7]
15	101.325	0[8][9]	ICAO's ISA,[8] ISO 13443,[9] EEA,[10] EGIA[11]
20	101.325		EPA,[12] NIST[13]
25	101.325		EPA[14]
25	100.000		SATP[15]
20	100.000	0	CAGI[16]
15	100.000		SPE[17]
20	101.3	50	ISO 5011[18]
°F	psi	% RH	
60	14.696		SPE,[17] U.S. OSHA,[19] SCAQMD[20]
60	14.73		EGIA,[11] OPEC,[21] U.S. EIA[22]
59	14.503	78	U.S. Army Standard Metro[23][24]
59	14.696	60	ISO 2314, ISO 3977-2[25]
°F	in Hg	% RH	
70	29.92	0	AMCA,[26][27] air density = 0.075 lbm/ft³. This AMCA standard applies only to air.

From http://en.wikipedia.org/wiki/Standard_conditions_for_temperature_and_pressure

Oxidizing atmosphere

Oxygen has been called the "ultimate oxidant" [1]
Accepts electrons readily (oxidation state goes down)

Organic matter is the "ultimate reductant" [1]
Donates electrons readily (oxidation state goes up)

→ Organic carbon will be oxidized in the atmosphere (ultimately end-product is CO_2)

(…as will most other elements)

[1] Morel and Hering, *Principles and Applications of Aquatic Chemistry* (Wiley, 1993)

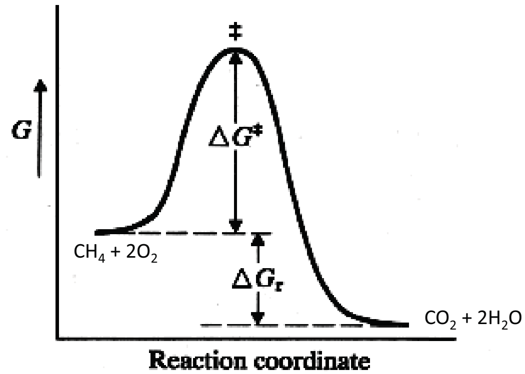
Oxidation: Thermodynamics

$$CH_4 + 2O_2 \rightarrow CO_2 + 2\ H_2O$$

molecule	ΔH_f^0 (kJ/mol)	S^0 (J/mol/K)
CH_4	-74.8	186.2
H_2O	-241.8	188.7
CO_2	-393.5	213.6
O_2	0.0	205.0

Thermodynamics vs. Kinetics

Spontaneity of a reaction (thermodynamic favorability) tells us ***almost nothing*** about the rate of a reaction (kinetic favorability)!



$5/2\ O_2 + N_2 + H_2O \rightarrow 2\ HNO_3$

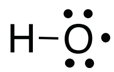
"We see from the large negative free energy of formation of nitric acid that it should be producible directly from its elements. Even starting with water and air, we see by our equation that nitric acid should form until it reaches a concentration of about 0.1 M where the calculated equilibrium exists. **It is to be hoped that nature will not discover a catalyst for this reaction, which would permit all the oxygen and part of the nitrogen of the air to turn the oceans into dilute nitric acid.**"

Free radicals

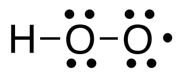
Chemical species that have an unpaired electron (unfilled outer shell)

→ *Very* reactive, and drive most of atmospheric chemistry

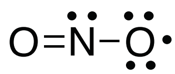
`



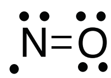
Hydroxyl radical (OH)



Hydroperoxy radical (HO_2)



Nitrogen dioxide (NO_2)

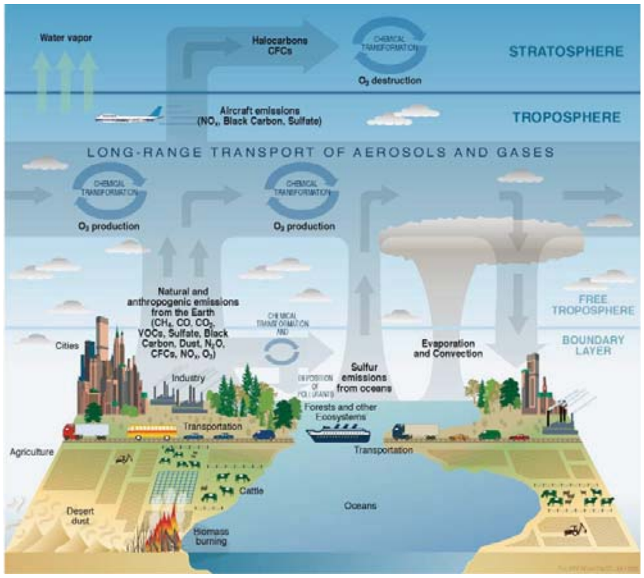


Nitrogen oxide (NO)

What's next

September	4	W	Introduction; atmospheric composition	1-38	
	9	M	Chemical kinetics 1: Reaction rates	75-93	
	11	W	Chemical kinetics 2: Reaction mechanisms	"	
	16	M	Photochemistry and spectroscopy 1	98-135	
	18	W	Photochemistry and spectroscopy 2	"	
	23	M	Temperature, pressure, radiance	720-734	PSet 1

Chemistry of the atmosphere



This image is in the public domain.

Strategic Plan for the U.S. Climate Change Science Program, 2006