Lecture 2: Introduction to Atmospheric Chemistry -- Part II

<u>Required</u> Reading: FP Chapter 1 & 2

Additional Reading: SP Chapter 1 & 2

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2005
Prof. Jose-Luis Jimenez

A flavor about the main problems

- London smog
  - Primary pollutants
- Photochemical ("LA") smog
- Global tropospheric pollution
- Stratospheric ozone depletion
- Acid deposition
- Particles
  - Health
  - Visibility
- Global climate change

Background O_3 Concentrations

From FP&P

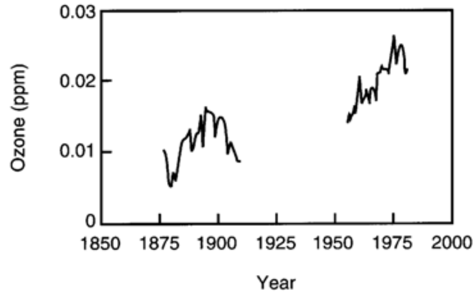


FIGURE 1.6 Typical tropospheric ozone concentrations in the 1800's and present values (adapted from Volz and Kley, 1988).

- <u>Tropospheric</u> O_3
  - "Bad ozone," effects on humans, plants, materials
- Roughly same chemistry as LA smog
- Globally increasing trend
  - Thought to be due to shift in chemical regime as NO_x has increased

Stratospheric Ozone

From FP&P

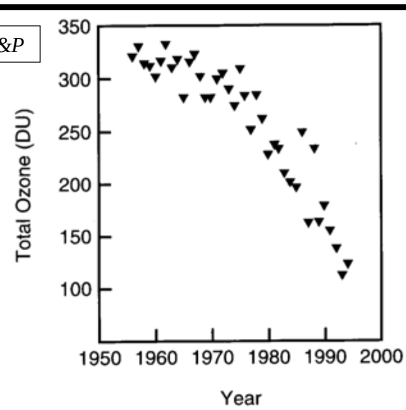


FIGURE 1.7 Average total column ozone measured in October at Halley Bay, Antarctica, from 1957 to 1994 (adapted from Jones and Shanklin, 1995).

- Stratospheric O3
  - "Good ozone": nothing to be damaged up there, protects us from hard UV radiation

- Discovered from ground measurements, even though there were satellite measurements!

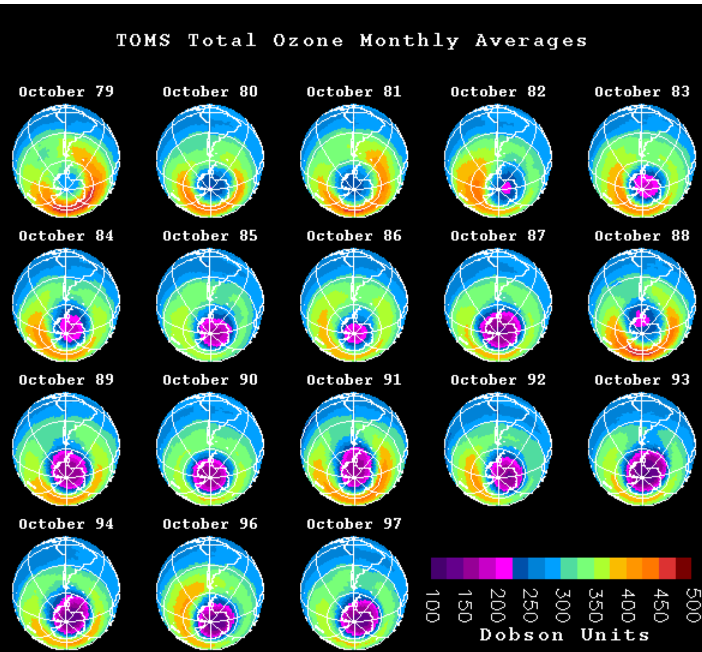


Fig. from S. Nidkorodov, UCI

Ozone Hole Evolution

Chemical Origin of O_3 Hole

- After O_3 hole discovery
  - Many theories: mixing, dynamics, chemistry…
- Chemical measurements proved involvement of chlorine chemistry
- Predicted by Molina + Rowlen (1974)
  - Nobel Prize 1995
  - Many unexpected details

From FP&P

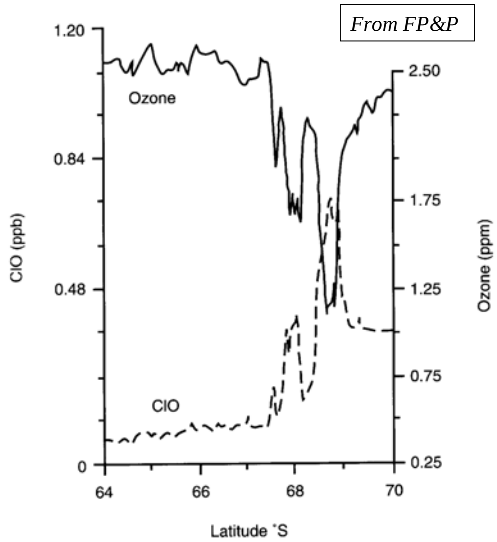
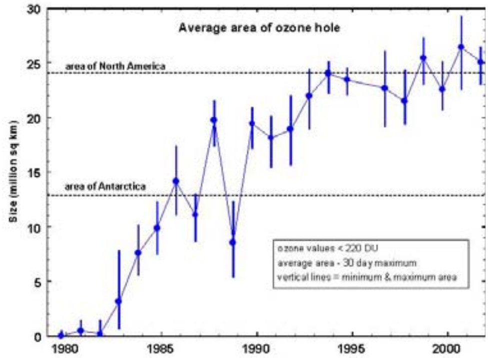
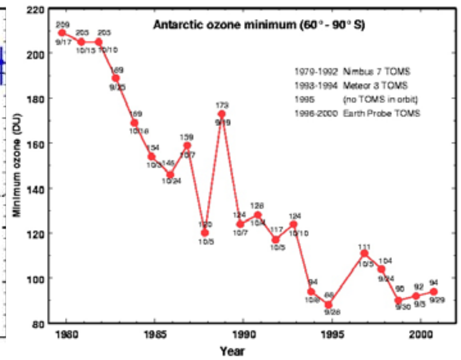


FIGURE 1.8 Measured concentrations of the chlorine monoxide free radical (ClO) as well as O_3 outside and inside the polar vortex on August 23, 1987 (adapted from Anderson, 1989).

Status of O_3 Hole





- Stabilized <u>due to</u> human action
  - Control and elimination of CFCs
- Not a “hot” research problem now, still many interesting questions

Figs. from S. Nidkorodov, UCI

Acid Deposition

pH

SO_4^{2-}

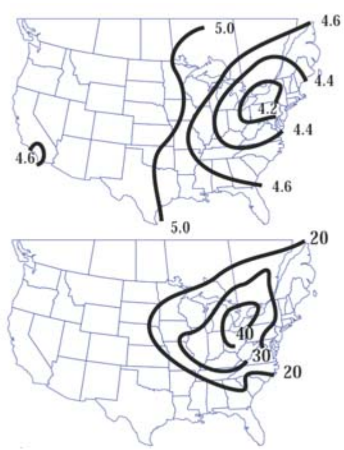


Figure 13-2 Regions of North America with low soil alkalinity to neutralize acid rain.

From Jacob

- pH of rain decreases, mostly due to H_2SO_4
- Dire effects if soil cannot neutralize acids

Health Effects of Particles I

From FP&P

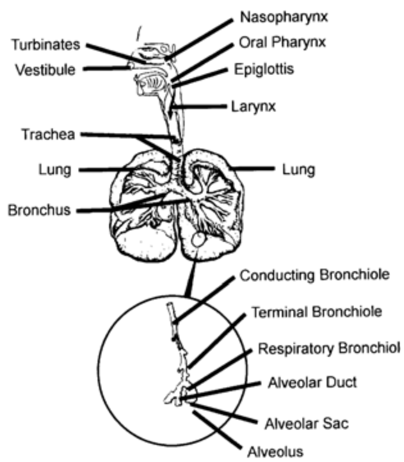


FIGURE 2.12 Schematic diagram of human respiratory tract. (From Hinds, W. C. *Aerosol Technology*. Copyright © 1982 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

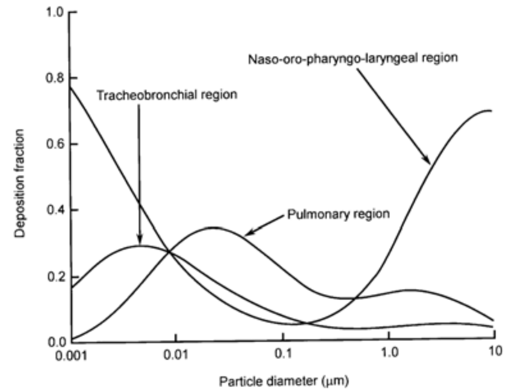


FIGURE 2.13 Calculated deposition of particles in various regions of the lung for polydisperse aerosol (σ_g = 2.5; see Chapter 9.A.2) (adapted from Yeh *et al.*, 1996).

- Submicron and ultrafine part. penetrate most deeply

Health Effects of Particles II

From FP&P

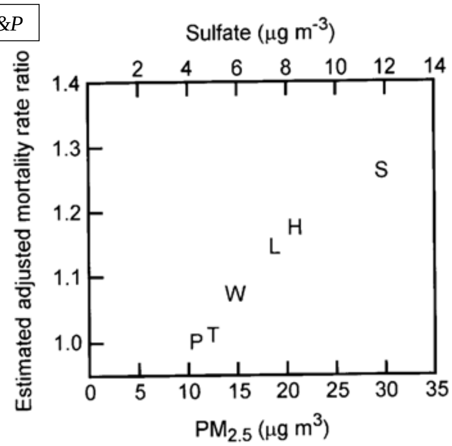


FIGURE 2.14 Estimated adjusted mortality rate ratios, taking the least polluted city, Portage, Wisconsin (P), as 1.0. T = Topeka, Kansas; W = Watertown, Massachusetts; L = St. Louis, Missouri; H = Harriman, Tennessee; S = Steubenville, Ohio. (Adapted from Dockery *et al.*, 1993.)

- "Harvard six-city study" (1993)
- Mortality increases with fine particle concentration
- Disputed for a decade, now considered proven
- Mechanism still uncertain

Visibility Degradation I

- Particles can scatter and absorb radiation
- These effect limit atmospheric visibility

From Jacob

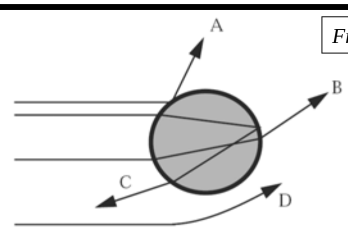


Figure 8-3 Scattering of a radiation beam: processes of reflection (A), refraction (B), refraction and internal reflection (C), and diffraction (D).

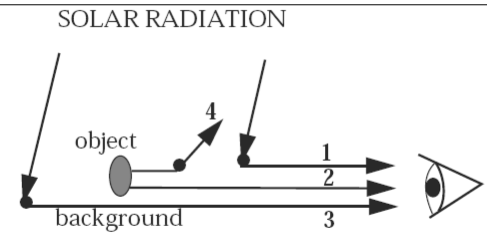


Figure 8-5 Reduction of visibility by aerosols. The visibility of an object is determined by its contrast with the background (2 vs. 3). This contrast is reduced by aerosol scattering of solar radiation into the line of sight (1) and by scattering of radiation from the object out of the line of sight (4).

Visibility Degradation II

- Scattering efficiency is very strong function of particle size
  - For a given wavelength
- Visible: $\lambda \sim 0.5\ \mu m$
- Particles 0.5-2 μm are

most efficient scatterers!

From Jacob

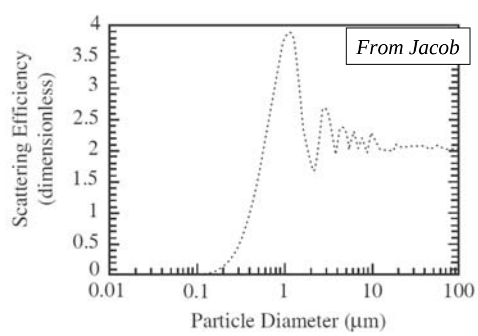


Figure 8-4 Scattering efficiency of green light ($\lambda = 0.5\ \mu m$) by a liquid water sphere as a function of the diameter of the sphere. Scattering efficiencies can be larger than unity because of diffraction. Adapted from Jacobson, M.Z., *Fundamentals of Atmospheric Modeling*, Cambridge University Press, Cambridge, 1998.

Earth's Radiation Balance

From FP&P

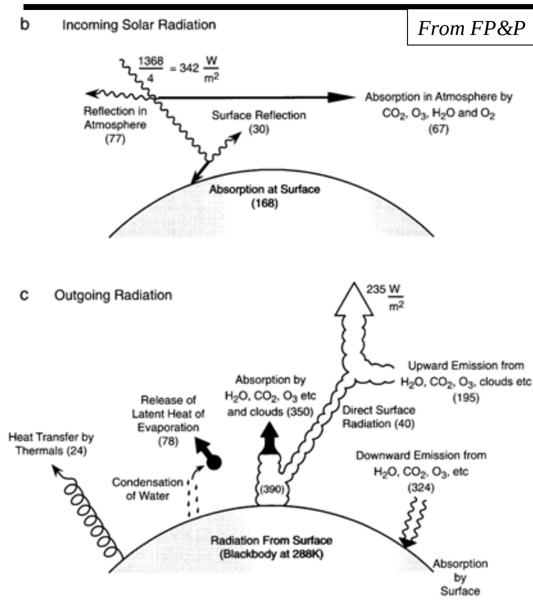


FIGURE 1.9 Global average mean radiation and energy balance per unit of earth's surface [adapted with permission from IPCC (1996) with numbers from Kiehl and Trenberth (1997)].

- Climate = average weather
- Driven by solar radiation
- Depends on complex balance of many terms
- Current: "small" perturbations in gas absorption causing heating

Greenhouse gas concentrations

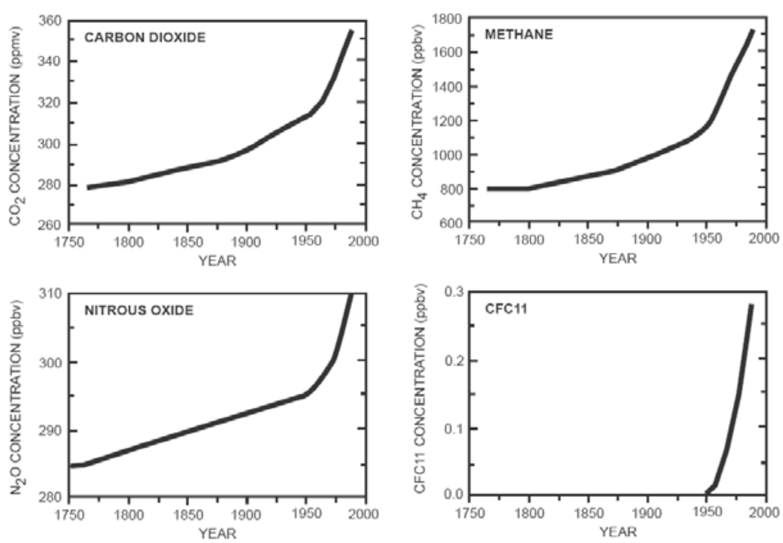
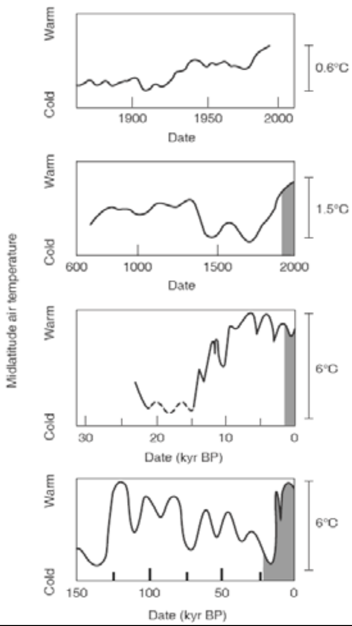


Figure 7-1 Rise in the concentrations of greenhouse gases since the 18th century

From Jacob

Earth's Temperature History



- Surface T as surrogate of climate
- Very large changes in past
- Current consensus is that recent changes are due to human activity
- Forcing system in unknown domain
  - danger of abrupt large changes in future (not quite like in "the day after tomorrow")

Figure 7-2 Trend in the surface temperature of the Earth at northern midlatitudes over the past 150,000 years. Each panel from the top down shows the trend over an increasingly longer time span, with the shaded area corresponding to the time span for the panel directly above. The record for the past 300 years is from direct temperature measurements and the longer-term record is from various proxies. From Graedel, T.E., and P.J. Crutzen, *Atmospheric Change: an Earth System Perspective*, New York: Freeman, 1993.

From Jacob

Problems are often linked!

TABLE 1.4 Atmospheric Effects[a] of Trace Gases

Gas	Urban Air Pollution	Acid Deposition	Visibility Impairment	Greenhouse Effect	Stratospheric O_3 Depletion	Decreased Self-Cleaning of Atmosphere (Decreases OH)
CO_2				+	+/−	
CH_4				+	+/−	+/−
CO	+					+
N_2O				+	+/−	
NO_x ($NO + NO_2$)	+	+	+		+/−	−
SO_2	+	+	+	−		
CFCs				+	+	
O_3	+	+		+		−

[a]Plus signs indicate a contribution to the effect; minus signs indicate amelioration. Dual signs (+/−) indicate that the effect of the gas can vary. For example, CO_2, N_2O, and NO_x can either enhance or deplete stratospheric O_3 depending on altitude. CH_4 generally ameliorates stratospheric O_3 depletion, except in the polar ozone hole. The tendency of CH_4 to diminish the self-cleaning of the atmosphere by reducing OH abundance is different in the Northern (NH) and Southern Hemispheres (SH); CH_4 diminishes self-cleaning in the SH but has the opposite effect in the NH.

Source: Graedel and Crutzen (1989).

From S&P