

# Lecture 22: Atmospheric Chemistry and Climate

*Required Reading: FP Chapter 14 (only sections that I cover)*

*Suggested Introductory Reading: Jacob Chapter 7*

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

## Introduction

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- *Climate: long-term statistical average of weather*

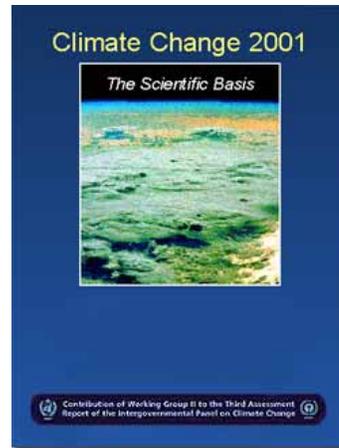
### Lecture Outline

- A. Radiation balance as driver for climate
- B. Greenhouse gases
- C. Aerosols

- Caveats:
  - Once more, one could teach an entire course on this topic, so we will only cover the main points
  - There is a lot more to Climate Change than atmospheric chemistry!
    - Atmospheric circulation / dynamics, ocean circulation and chemistry, precipitation, sea level, regional differences...
  - But changes in atmospheric chemistry are the driver of CC

## IPCC Report

- To learn more, see IPCC report
  - “TAR”, third assessment report
  - Available online for free  
[http://www.grida.no/climate/ipcc\\_tar/wg1/](http://www.grida.no/climate/ipcc_tar/wg1/)
    - Link on class page
- “*The bible of climate change*”
  - It's big and thick
  - It was written by a committee
  - It deals with cataclysmic events such as floods and droughts
  - No one reads it from cover to cover
  - You can open it up on any page and find something interesting
  - It is full of internal contradictions
  - It has its true believers and its rabid skeptics  
*(from Steve Schwartz, DOE Brookhaven Nat Lab)*

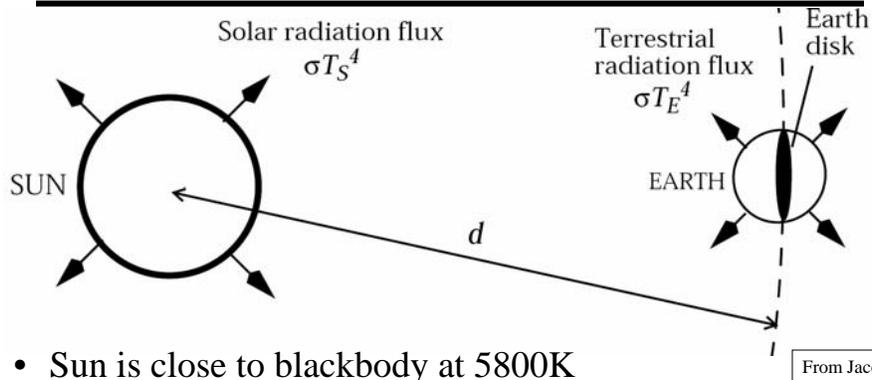


Another report “FAR”  
coming in ~2007

## Is Climate Change Happening?

- IPCC 1995 (SAR)
  - “The balance of evidence suggests a discernible human influence on global climate”
- IPCC 2001 (TAR)
  - “In the light of new evidence and taking into account the remaining uncertainties, most of the observed warming over the last 50 years is likely to have been due to the increase in greenhouse gas concentrations”
- Pieter Tans (NOAA)
  - “with CO<sub>2</sub> increasing by 50% since preindustrial times, I can’t see how someone could think that climate would not have changed”
- Even the Bush administration agrees that CC is happening
- Real question is the magnitude and region/ temp. patterns

## Radiative Balance of the Earth I



- Sun is close to blackbody at 5800K
- Power emitted by blackbody:  $E = \sigma T^4$ 
  - $\sigma$  is Stefan-Boltzmann constant =  $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
  - Sun emits  $\sim 64 \text{ MW m}^{-2}$
- Total power emitted by sun:  $E_s = 4\pi R_s^2 \sigma T^4$ 
  - $E_s \sim 4 \times 10^{26} \text{ W}$  Distributed uniformly in all directions

## Radiative Balance of the Earth II

- Power density at any distance from the sun

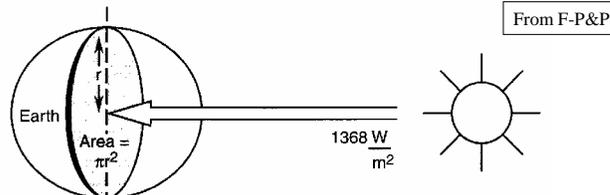
- $R_s = 7 \times 10^5 \text{ km}$
- $d = 1.5 \times 10^8 \text{ km}$

$$F_s = \frac{E_s}{4\pi d^2} = \frac{4\pi R_s^2 \sigma T_s^4}{4\pi d^2} = \frac{\sigma T_s^4 R_s^2}{d^2}$$

- Substituting we get:

$$F_s = 1397 \text{ W m}^{-2} \text{ (actually 1368)}$$

- That is power in Earth's plane:



- On average the power over the Earth's surface:

$$F'_s = F_s \frac{\pi R_E^2}{4\pi R_E^2} = \frac{F_s}{4} = 342 \text{ W m}^{-2}$$

## Radiative Balance of the Earth III

- Simplest case: no atmosphere, complete absorption

- In thermal equilibrium Earth would reradiate same amount

$$\Delta E = 0 \Rightarrow F'_s = F_E$$

$$F_E = \sigma T_E^4 = 342 \text{ W m}^{-2}$$

$$T_E = 279 \text{ K (observed 288K)}$$

- Life is not so simple!

- Albedo = 31% from satellites
  - Fraction of incoming solar radiation reflected back to space
  - $107 \text{ W m}^{-2}$  is just reflected
  - So real emission from Earth is smaller =  $342 - 107 = 235 \text{ W m}^{-2}$

$$F'_s = F_s(1-A) = 235 \text{ W m}^{-2}$$

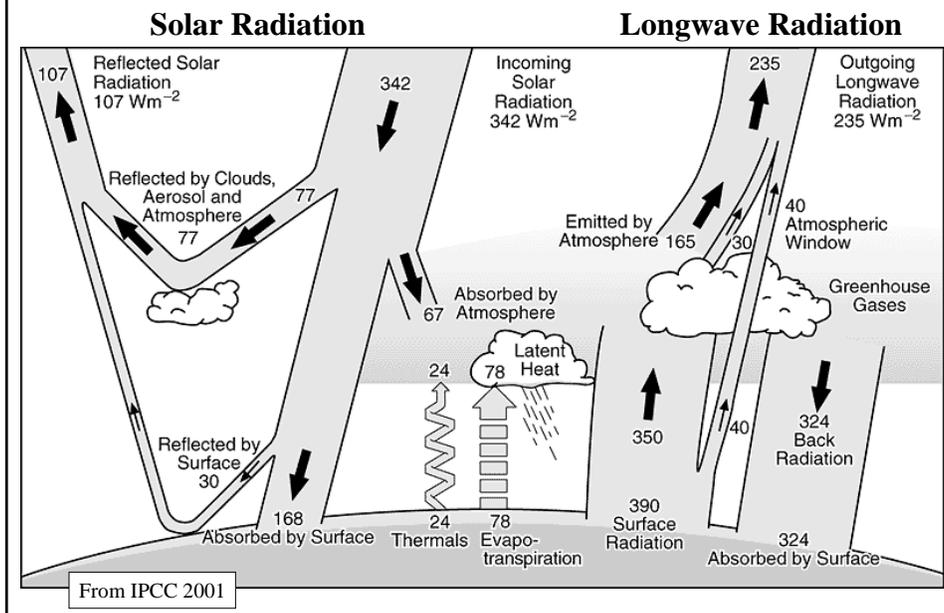
$$F_E = \sigma T_E^4 = 235 \text{ W m}^{-2}$$

$$T_E = 254 \text{ K (way too cold!)}$$

- Reality

- Atmosphere absorbs radiation
- 254 K is “effective T” of Earth-Atmosphere system (T @ 5.5 km)

## The Real Radiative Balance of the Earth



## Earth's Surface is not Uniform

- More absorption at tropics
- More emission at poles
- On average  $\Delta E = 0$  at each location!

$$E_{short} + E_{long} + E_{transport} = 0$$

- This energy transport is what drives the large scale atmospheric circulation (Hadley, etc.)

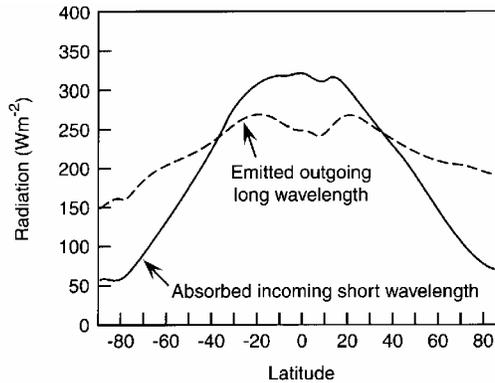
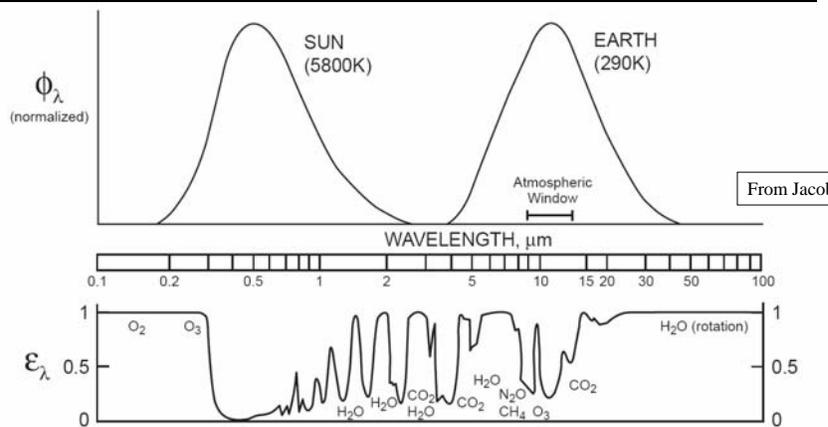


FIGURE 14.5 Annual mean radiation measured by satellite in 1988 at the top of the atmosphere as a function of latitude for incoming absorbed short-wavelength radiation and emitted outgoing long-wavelength radiation (adapted from Trenberth and Solomon, 1994).

From F-P&P

## Wavelength Dependence



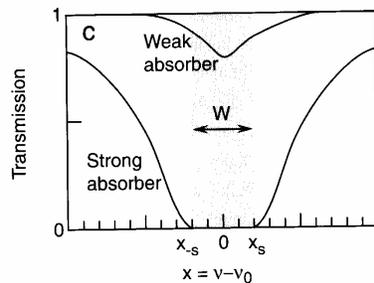
From Jacob

Figure 7-11 Efficiency of absorption of radiation by the atmosphere as a function of wavelength. Major absorbers are identified.

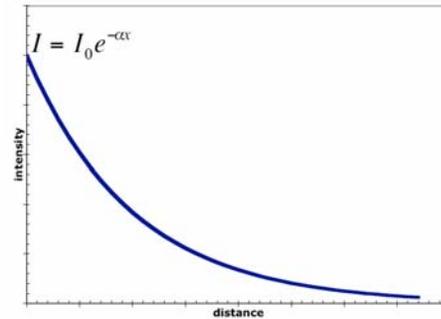
- Transparent in visible and atmospheric window
- Also e.g. @ 4  $\mu\text{m}$ , but we don't care!

## Saturation of Absorption at a Certain $\lambda$

- Weak absorption:  $\alpha C$
- Stronger:  $\alpha \sqrt{C}$
- Saturated:  $\alpha \log C$ 
  - C is gas concentration



- Beer's Law absorption



<http://www.orc.soton.ac.uk/~wsb/phys1004/lectures/04/lecture%205%20202004.pdf>

FIGURE 14.8 (a) Meaning of equivalent width,  $W$ ; (b) Doppler and Lorentzian line-shapes for equivalent half-widths; (c) transmission curves for an absorption line for a weak and strong absorber, respectively (adapted from Lenoble, 1993).

From F-P&P

## Potential Greenhouse Gases

- Four conditions for a greenhouse gas to be important:
  - Strong absorption cross section
  - Large enough concentration
  - Long lifetime
  - Absorb in the atmospheric window
- H<sub>2</sub>O 60%, CO<sub>2</sub> 26%, O<sub>3</sub> 8%
- Enhanced greenhouse effect:
  - CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, O<sub>3</sub>, CFCs, HCFCs, SF<sub>6</sub>

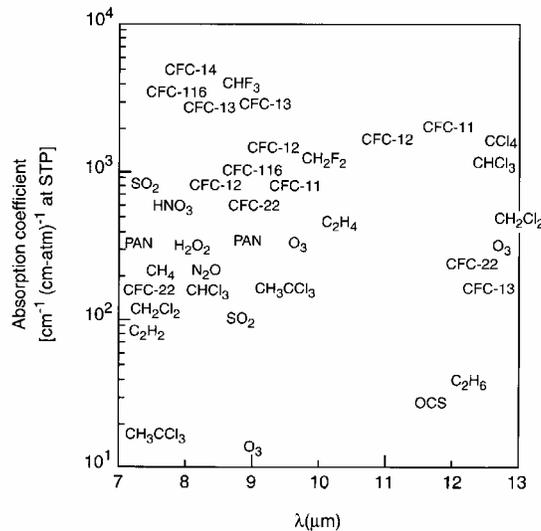
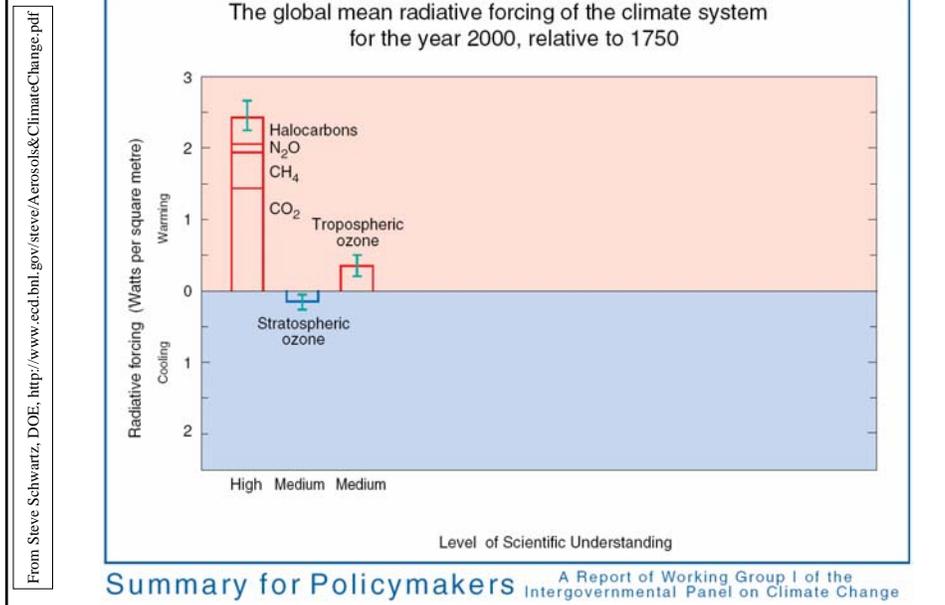


FIGURE 14.10 Intrinsic infrared absorption band strengths of some potential greenhouse gases in the atmospheric "window" (from Ramanathan, 1988a, 1988b).

From F-P&P

## Summary of GHG Forcings



## Radiative Forcing ( $F$ )

- $F$ : change in radiation @ tropopause due to increase in a greenhouse gas
  - Use the tropopause because surface + troposphere are tightly coupled by convection and mixing
  - Tropospheric absorption leads to stratospheric cooling (less radiation to absorb)
- Climate change per unit RF?
  - Use average surface T as proxy for climate
$$\Delta T = \lambda F$$
  - $\lambda$ : climate sensitivity, K / (W/m<sup>2</sup>)
  - Black body at 255 K, ~0.27 K / (W/m<sup>2</sup>)
  - Range of estimates from models: 0.3-1.1 K / (W/m<sup>2</sup>)

## The Earth's Climate Sensitivity

- **What is Earth's climate sensitivity?**

- *National Academy Report (Charney, 1979):*

$$F = 4 \text{ W m}^{-2}$$

“ We estimate the most probable global warming for a doubling of CO<sub>2</sub> to be *near 3 degrees C*, with a probable error of *plus or minus 1.5 degrees*.

- *Intergovernmental Panel on Climate Change (IPCC, 2001):*

“ Climate sensitivity [to CO<sub>2</sub> doubling] is likely to be in the range *1.5 to 4.5°C*.

*This level of uncertainty is not very useful for policy planning.*

From Steve Schwartz, DOE, <http://www.ecd.bnl.gov/steve/Aerosols&ClimateChange.pdf>

## CO<sub>2</sub> Atmospheric Increase: 1958 on

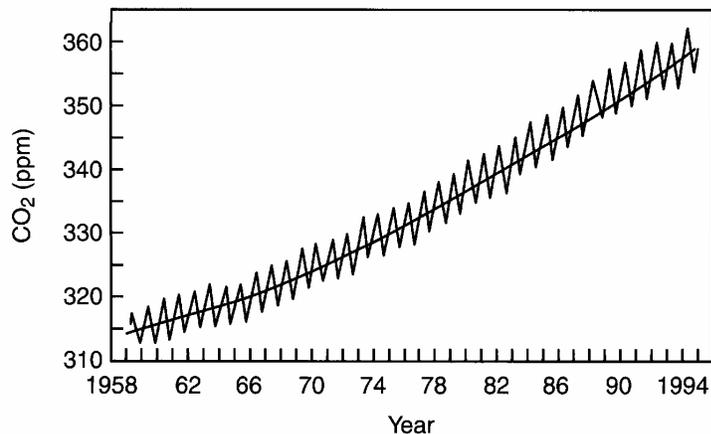


FIGURE 14.12 Measured CO<sub>2</sub> concentrations at Mauna Loa, Hawaii, from 1958 to 1994. The line represents the atmospheric CO<sub>2</sub> expected if 55.9% of the cumulative emissions of CO<sub>2</sub> from fossil fuel combustion and cement production remained in the atmosphere (adapted from Keeling *et al.*, 1995).

From F-P&P

## CO<sub>2</sub> Atmospheric Increase: last 40,000 years

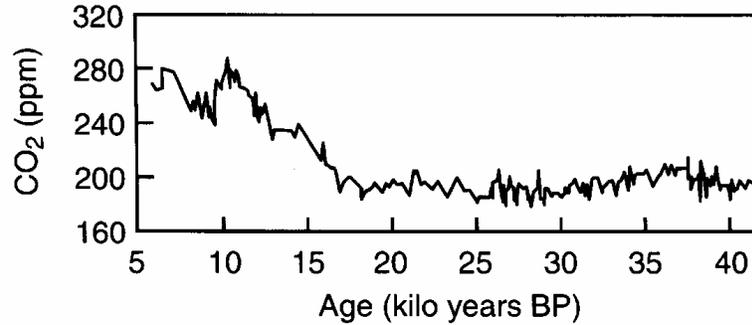
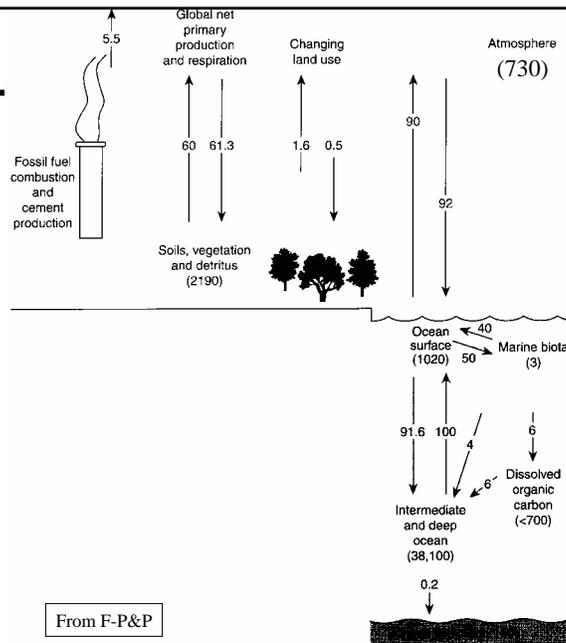


FIGURE 14.13 Concentrations of atmospheric CO<sub>2</sub> measured using gases trapped in ice cores from Byrd Station, Antarctica, from 5000 to 40,000 years before the present (bp) (adapted from Anklin *et al.*, 1997).

From F-P&P

## C Cycle

- Very large fluxes between atmosphere and soils / oceans
- Oceans are the major reservoir
  - From acid rain lecture: Henry's law +  $\text{HCO}_3^- + \text{CO}_3^{2-}$
  - Lowering ocean pH
  - Limited by ocean mixing => long timescales



From F-P&P

FIGURE 14.11 Summary of global carbon cycle. Amount (in gigatons of C =  $10^9$  metric tons =  $10^{15}$  g of C). Reservoirs are shown in parentheses, and fluxes (gigatons of C per year) are indicated by arrows. Note that the time scales associated with the various processes vary (adapted from IPCC, 1996).

# Trop. Warming vs. Strat. Cooling

- $\text{CO}_2$ 
  - Traps radiation in the lower troposphere
  - Radiates more effectively in the upper atmosphere
- Stratospheric cooling has been observed
  - Mostly due to lower strat.  $\text{O}_3$
  - Effects on dynamics,  $\text{O}_3$  absorption

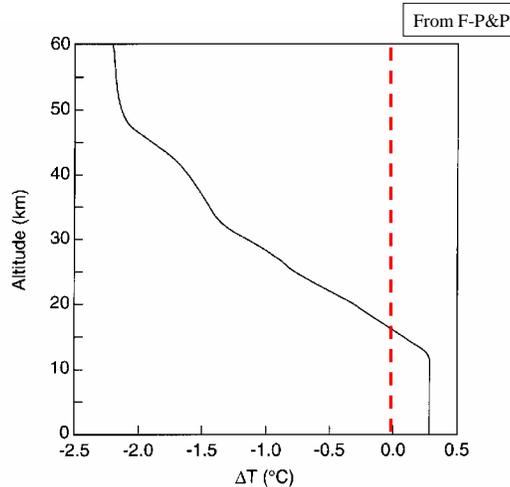
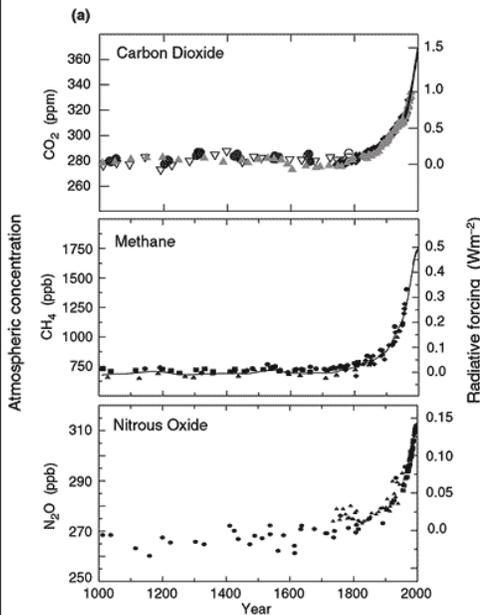
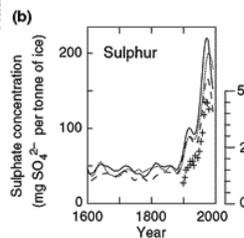


FIGURE 14.7 Model-calculated atmospheric temperature changes as a function of altitude due to an increase in  $\text{CO}_2$  from 315 ppm in 1960 to 370 ppm projected for 2000 (no feedbacks taken into account) (adapted from Rind and Lacis, 1993).

# Increase of Other Constituents



- Not just  $\text{CO}_2$  but also  $\text{CH}_4$  and  $\text{N}_2\text{O}$  have increased rapidly
- Also S from sulfate aerosols
  - More later



From IPCC 2001

# CH<sub>4</sub> increase and budget

TABLE 14.1 Estimated Methane Sources during the Mid-1980s<sup>a</sup>

Source	Emissions (Tg of C/year) <sup>b</sup>
Natural	260 ± 30
Anthropogenic	370 ± 40
Gas leakage and oil production	85-105
Coal mining	25-45
Rice fields	20-150
Ruminants	65-100
Biomass burning	20-60
Animal wastes	20-40
Sanitary landfills	20-60

<sup>a</sup> From Crutzen (1995).  
<sup>b</sup> Tg of C = 10<sup>12</sup> g of C.

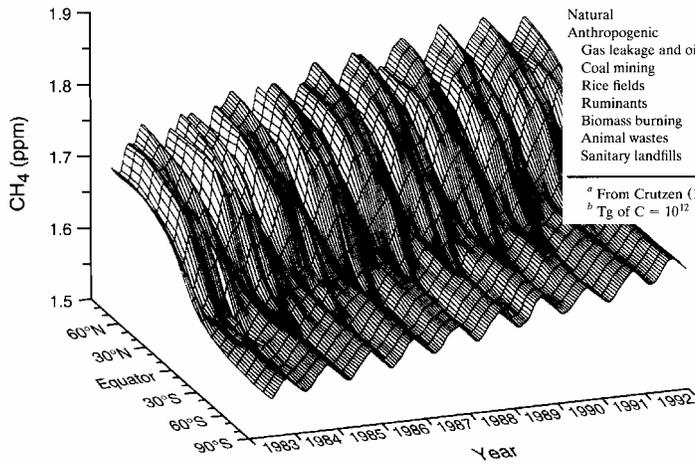
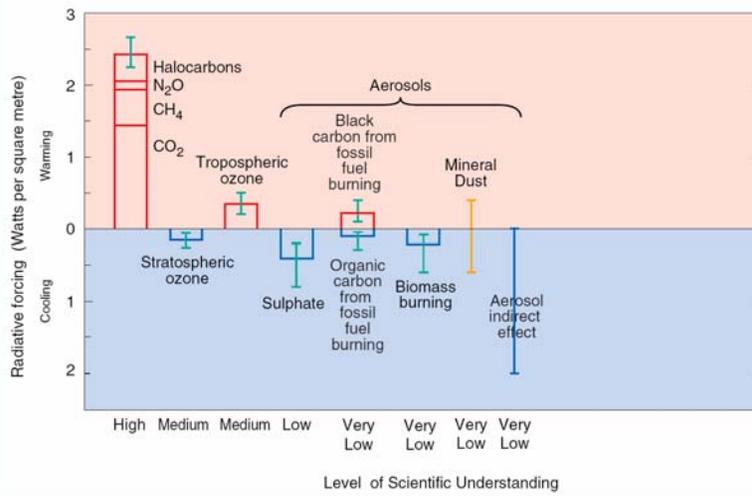


FIGURE 14.16 Averaged 3-D methane concentrations in the marine boundary layer. Lines are arc guides for the eye (adapted from Dlugokencky *et al.*, 1994a).

From F-P&P

# Summary of GHGs and Aerosols

The global mean radiative forcing of the climate system for the year 2000, relative to 1750



From Steve Schwartz, DOE, <http://www.eed.hnl.gov/steve/Aerosols&ClimateChange.pdf>

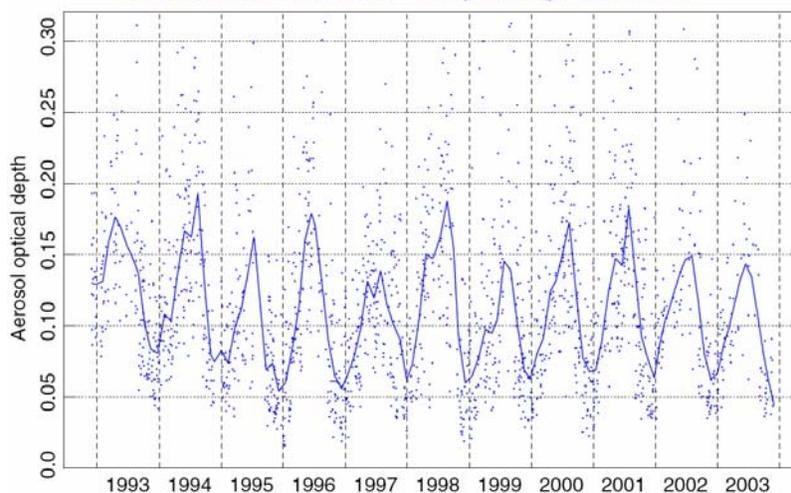
Summary for Policymakers A Report of Working Group I of the Intergovernmental Panel on Climate Change

## Aerosol Effects

- *Physical basis already covered in lecture 20*
- Very uncertain because of
  - Short lifetime
  - Very incomplete data
  - Great complexity of sizes & compositions
- “Direct effect”
  - Aerosols scatter sunlight back to space => cooling
    - Black carbon absorbs => warming
  - Most efficient when  $d_p \sim \lambda$  (submicron aerosols)
  - Same physics that cause visibility degradation
  - All aerosol constituents participate in scattering
    - If they absorb water, they scatter more

## Aerosol Variability

Determined by sunphotometry  
North central Oklahoma - Daily average at 500 nm



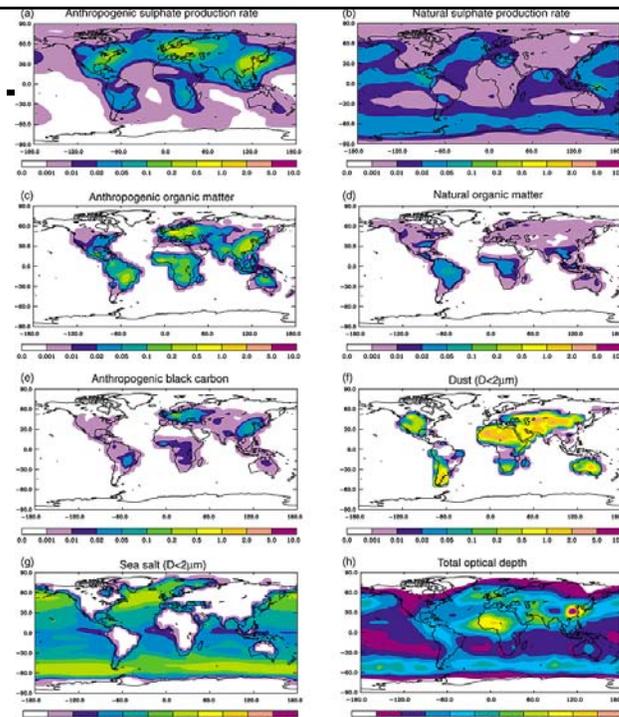
From Steve Schwartz, DOE, <http://www.ecd.hnl.gov/steve/Aerosols&ClimateChange.pdf>

*J. Michalsky et al., JGR, 2001*

*Variability is due to variability in tropospheric aerosols.  
Optical depth variability of 0.1 is common even at a rural mid-continental site.*

## Aerosol production rates for most important aerosol types

From IPCC 2001  
[http://www.grida.no/climate/ipcc\\_tar/wg1/fig5-2.htm](http://www.grida.no/climate/ipcc_tar/wg1/fig5-2.htm)



## Aerosol “Indirect” Effects

- Clouds are formed when water condenses on preexisting aerosol
  - *Activation & Kohler theory in Lecture 20*
  - Clouds both reflect and absorb large amounts of radiation (slide 8)
  - If aerosol changes, cloud can change
    - E.g. “Twomey effect” or “1<sup>st</sup> indirect effect”
      - More particles
      - Same H<sub>2</sub>O
      - Smaller droplets
      - Closer to solar wavelengths, so more scattering => cooling

# Many indirect effects!

## *Indirect Shortwave Radiative Effects—Aerosols influence cloud properties*

- More droplets → Brighter clouds (Twomey)
- More droplets → Enhanced cloud lifetime (Albrecht)
- More droplets → Narrowing of drop distribution -- warming (Liu)

## *Semi-Direct Shortwave Radiative Effect*

Absorbing aerosol heats air and evaporates clouds (Hansen)

## *Longwave Radiative Effect (Clear sky)*

Greenhouse effect of aerosol particles (Vogelmann)

## *Hydrological Effects*

- Suppressed surface evaporation -- Spinning down the water cycle
- Displaced precipitation -- Clouds last longer or evaporate (Rosenfeld)

From Steve Schwartz, DOE, <http://www.ecd.bnl.gov/steve/Aerosols&ClimateChange.pdf>

Additional reading: Global indirect aerosol effects: a review. U. Lohmann and J. Feichter. Atmos. Chem. Phys., 5, 715–737, 2005. <http://www.atmos-chem-phys.org/acp/5/715/>

