Atmospheric Composition & Climate I

Required Reading: Jacob Chapter 7

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

Business Items

• HW#6 due tomorrow 9:30 am
  – Skype screenshare to help w code (during office hrs)
  – 6.3c: radicals are very high, timesteps short
• HW#7 assigned tomorrow (aerosols, climate)
• Midterm will be returned on Tue
• Questions?
Introduction

• *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 composition are the driver of CC

IPCC Reports

• To learn more, see IPCC report WG1
  – “FAR”, 4th assessment report
  – Available online for free
    • 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)

5th report will be released in late Sep. 2013
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”

- IPCC 2007 (AR4)
  - “Warming of the climate system is unequivocal, as is now evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global average sea level”

- Pieter Tans (NOAA)
  - “with CO₂ increasing by 50% since preindustrial times, I can’t see how someone could think that climate would not have changed”

- Even the Bush administration agreed that CC is happening
  - Just argued that it was too expensive to do something about it

- Real question is the magnitude and region / temp. patterns
  - And the real real question is what will humanity do about it? (Sagan vs Mayr)

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 = $5.67 \times 10^{-8}$ W m⁻² K⁻⁴
  - Sun emits ~ 64 MW m⁻²
- Total power emitted by sun: $E_s = 4\pi R_s^2 \sigma T^4$
  - $E_s \sim 4 \times 10^{26}$ W Distributed uniformly in all directions

From Jacob
Radiative Balance of the Earth II

- Power density at any distance from the sun
  - \( R_s = 7 \times 10^5 \text{ km} \)
  - \( d = 1.5 \times 10^8 \text{ km} \)
- Substituting we get:
- That is power in Earth’s plane:

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

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

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

\[
F_s' = F_s \frac{\pi R_E^2}{4\pi R_s^2} = \frac{F_s}{4} = 342 \text{ W m}^{-2}
\]

Q: how do we estimate \( T \) of Earth if there was no atmosphere?

Radiative Balance of the Earth III

- Simplest case: no atmosphere, complete absorption
  - In thermal equilibrium Earth would reradiate same amount
- Life is not so simple!
  - Albedo = 31% from satellites
    - 107 W m\(^{-2}\) is just reflected
    - So real emission from Earth is smaller = 342 – 107 = 235 W m\(^{-2}\)

\[
\Delta E = 0 \Rightarrow F_s' = F_E
\]

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

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

Amount of solar radiation reflected during September 2008. Along the equator, clouds reflected a large proportion of sunlight, while the pale sands of the Sahara caused the high reflectiveness in North Africa. Neither pole is receiving much incoming sunlight at this time of year, so they reflect little energy even though both are ice-covered. (NASA map by Robert Simmon, based on data.)

Radiative Balance of the Earth IV

• Let’s calculate the new effective temperature

\[ F_s' = F_s(1-A) = 235 \text{ W m}^{-2} \]
\[ F_E = \sigma T_E^4 = 235 \text{ W m}^{-2} \]
\[ T_E = 254 \text{ K (way too cold!)} \]

Distribution of thermal infrared radiation emitted by Earth in September 2008. Most heat escaped from areas just north and south of the equator, where the surface was warm, but there were few clouds. Along the equator, persistent clouds prevented heat from escaping. Likewise, the cold poles radiated little heat. (NASA map by Robert Simmon, based on CERES data.)


• Q: What is going on? Can this be correct?
  A. It is correct but the interpretation needs to be nuanced
  B. There is a logical flaw in the argument
  C. Jose must have made a mistake with Igor
  D. I don’t know

Surface & Atmosphere Energy Budgets

• “Net” thermal radiation is the difference of two large numbers (next slide)

Earth’s Surface is not Uniform

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

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

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

- Clicker Q: what wavelength (μm) leads to climate change the most?
  A. 0.4-1  B. 2-2.5  C. 3-5  D. 9-13  E. Dunno

Saturation of Absorption at a Certain λ

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

Beer’s Law absorption

From F-P&P

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).
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
- \( H_2O \) 60%, \( CO_2 \) 26%, \( O_3 \) 8%
- Enhanced greenhouse effect:
  - \( CO_2, N_2O, CH_4, O_3, CFCs, HCFCs, SF_6 \)

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

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E.g. of minor greenhouse gas


**NF_3, the greenhouse gas missing from Kyoto**

Michael J. Prather^1 and Juno Hsu^1

- 2008 production \( \sim 4,000 \) tons
- the 100 year GWP, relative to carbon dioxide, is 17200
- Equivalent to 67 Mtons of \( CO_2 \)
- Q: does NF_3 absorb in the atmospheric window?

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### Atmospheric Composition (average)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N$_2$)</td>
<td>0.78</td>
</tr>
<tr>
<td>Oxygen (O$_2$)</td>
<td>0.21</td>
</tr>
<tr>
<td>Water (H$_2$O)</td>
<td>0.04 to &lt; 5x10$^{-3}$; 4x10$^{-6}$-strat</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>0.0093</td>
</tr>
<tr>
<td>Carbon Dioxide (CO$_2$)</td>
<td>370x10$^{-6}$ (date: 2000)</td>
</tr>
<tr>
<td>Neon (Ne)</td>
<td>18.2x10$^{-6}$</td>
</tr>
<tr>
<td>Ozone (O$_3$)†</td>
<td>0.02x10$^{-6}$ to 10x10$^{-6}$</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>5.2x10$^{-6}$</td>
</tr>
<tr>
<td>Methane (CH$_4$)</td>
<td>1.7x10$^{-6}$</td>
</tr>
<tr>
<td>Krypton (Kr)</td>
<td>1.1x10$^{-6}$</td>
</tr>
<tr>
<td>Hydrogen (H$_2$)</td>
<td>0.55x10$^{-6}$</td>
</tr>
<tr>
<td>Nitrous Oxide (N$_2$O)</td>
<td>0.32x10$^{-6}$</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>0.03x10$^{-6}$ to 0.3x10$^{-6}$</td>
</tr>
<tr>
<td>Chlorofluorocarbons</td>
<td>3.0x10$^{-9}$</td>
</tr>
<tr>
<td>Carbonyl Sulfide (COS)</td>
<td>0.1x10$^{-9}$</td>
</tr>
</tbody>
</table>

† Ozone has increased in the troposphere, but decreased in the stratosphere. [From Heald]

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**Increases of Major GH gases**

[From IPCC 2007, Ch6]
NOAA Greenhouse Gas Records

http://www.esrl.noaa.gov/gmd/aggi/

NOAA Greenhouse Gas Records

Radiative Forcings

A. Radiative forcing of climate between 1750 and 2005

<table>
<thead>
<tr>
<th>Radiative Forcing Terms</th>
<th>Climate efficacy</th>
<th>Spatial scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-lived greenhouse gases</td>
<td>1.0 (see reaction)</td>
<td>Global, High</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.0 ± 1.2</td>
<td>Global, High</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.5 ± 2.0</td>
<td>Continental to global, Med</td>
</tr>
<tr>
<td>Stratospheric water vapour from CH₄</td>
<td>~1.0</td>
<td>10 years, Global, Low</td>
</tr>
<tr>
<td>Ozone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface albedo</td>
<td>0.7 ± 1.1</td>
<td>Days, Continental to global, Med</td>
</tr>
<tr>
<td>Direct effect</td>
<td>1.0 ± 2.0</td>
<td>Hours, Continental to global, Low</td>
</tr>
<tr>
<td>Total Aerosol</td>
<td>~0.8</td>
<td>Hours, Continental, Low</td>
</tr>
<tr>
<td>Cloud albedo effect</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear contrails</td>
<td>0.7 ± 1.0</td>
<td>10 - 100 yrs, Global, Low</td>
</tr>
<tr>
<td>Solar insolation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. Timescale, Scientific understanding
Business Items

- No class on Tue 30-Apr
- Review session on Thu 2-May
- Exam on Thu 9\textsuperscript{th}, 9:30-11:30 am, room TBD
- Feedback survey later today, anonymous, total response counts for class participation
  - Any additional feedback is appreciated
- FCQs next week

Radiative Forcing & Climate Sensitivity

- $F$: 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\textsuperscript{2})
- Q: what is $\lambda$ for black body @ 255 K w/o atmosphere?
  A. 0.27  B. 0.35  C. 0.52  D. 1.1  E. D’n
Climate Models

- Range of estimates from models:
  - 0.3-1.1 K / (W/m^2)

From IPCC 2007, Ch1

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 CO₂ 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 CO₂ 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.

Greenhouse Gases and Climate of Past

The Eocene climate was warm, even at high latitudes:
- palm trees flourished in Wyoming
- crocodiles lived in the Arctic
- Antarctica was a pine forest
- deep ocean temperature was 12°C (today it is ~2°C)
- sea level was at least 100 meters higher than today

Present models cannot reproduce this warm climate – missing processes?
Positive feedbacks could cause abrupt climate change but this is not well understood

From Jacob
Atmospheric Composition & Climate II

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Atmospheric Chemistry
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Trop. Warming vs. Strat. Cooling

• CO₂
  – Traps radiation in the lower troposphere
  – Radiates more effectively in the upper atmosphere

• Stratospheric cooling has been observed
  – Mostly due to lower strat. O₃
  – Effects on dynamics, O₃ absorption

FIGURE 14.7 Model-calculated atmospheric temperature changes as a function of altitude due to an increase in CO₂ from 315 ppm in 1960 to 370 ppm projected for 2000 (no feedbacks taken into account) (adapted from Rind and Lacis, 1993).
Aerosol Variability

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

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

Rayleigh scattering: $D_p \ll \lambda$
Mie scattering: $D_p \approx \lambda$
Geometric scattering: $D_p \gg \lambda$

Size Parameter
$\alpha = \frac{\pi D}{\lambda}$
Scattering vs. size

- This is for a single particle
- Note Rayleigh limit as $d^6$ at small sizes

Q: what scatters more 520 nm light, 1 particle with $d = 1.7 \mu m$, or 1000 particles with $d = 0.17 \mu m$?

A. The 1.7 $\mu m$ particle
B. The $10^3 \times 0.17 \mu m$ particles
C. They scatter exactly the same amount of light
D. They scatter approximately the same amount of light
E. I don’t know

Mie Scattering per unit volume

- A single 10 $\mu m$ particle scatters much more than a 1 $\mu m$ particle
- But the reverse is true per unit volume (one 10 $\mu m$ particle vs 1000 1 $\mu m$ particles)
- By coincidence, mass concentration is largest for particles that are most efficient scatterers
- Scattering by fine mode dominates total scattering in most conditions
- Some exceptions such as dust storms
Q: why does water uptake enhance light scattering so much?

A. Because water scatters light strongly
B. Because water disperses the sulfate ions and causes them to scatter light more strongly
C. Because the particles coagulate
D. Because the particles grow
E. I don’t know

FIGURE 9.26 Calculated light scattering coefficient for NH$_4$HSO$_4$ droplets as a function of relative humidity (adapted from Stoane, 1986).

FIGURE 9.28 Size distribution of particle geometric cross section as a function of geometric diameter for a typical rural aerosol (adapted from Hegg et al., 1993).
Absorption by EC / BC

Q: why is black carbon black?

A. Many different vibrational modes for absorbing light
B. Many different rotational modes
C. Many different electronic states
D. Photons get captured by the grid
E. I don’t know

Climate Effects of BC
Sources of BC

Black carbon and co-emitted species by region and source in 2000

Revised estimate of BC forcing

Global climate forcing of black carbon and co-emitted species in the industrial era (1750 - 2005)
Activation of Aerosols into Cloud Droplets

$$\frac{P_{w,\text{part}}}{P_{w,\text{flat}}} = \exp \left( \frac{2\sigma}{R_p \rho_p T_r} - \frac{3M_{W_m}}{4\pi \rho_p M_W r^3} \right) = \exp \left( \frac{A}{r^3} - \frac{B}{r^3} \right)$$

First term: “Kelvin effect”
Second term: “Raoult or solute effect”

$$\frac{d}{dr} \left( \frac{P_{w,\text{part}}}{P_{w,\text{flat}}} \right) = 0 \Rightarrow r_c = \left( \frac{3B}{A} \right)^{1/2}$$

$$\ln \left( \frac{P_{w,\text{part}}}{P_{w,\text{flat}}} \right) = \ln(S_r + 1) \approx S_r = \left( \frac{4A}{27B} \right)^{1/2}$$

**Example:** Calculate the critical supersaturation of a 0.08 μm diameter ammonium sulfate particle

$$A = \frac{2\sigma}{\rho_p R_p T_r} = \frac{2(0.075 \times 8.315)}{1000 \times 0.461 \times 298} = 1.0919 \times 10^{-4} m$$

$$m_r = 4\pi \rho_r r_r^3 = 4\pi (1760 \times 0.04 \times 10^{-6}) m^3 = 4.7183 \times 10^{-7} kg$$

$$B = \frac{3M_{W_m}}{4\pi \rho_p M_W r} = \frac{3(0.018 \times 4.7183 \times 10^{-3})}{4\pi (1000 \times 0.132 \times 0.25)} = 4.608 \times 10^{-31} m^3$$

$$S_r = \left( \frac{4A}{27B} \right)^{1/2} = \left( \frac{4(1.0919 \times 10^{-4} m^2)}{27(4.608 \times 10^{-31} m^3)} \right)^{1/2} = 0.00295 \approx 0.2055 \Rightarrow RH = 1 + S_r = 100.205%$$

Adapted from Don Collins, Texas A&M U: Fig.: http://en.wikipedia.org/wiki/K%C3%B6hler_theory

**Example of Activation in a Cloud**

- The next set of slides shows the evolution of the size (i.e. water uptake) of two particles of initial dry sizes of 150 and 300 nm.
- As the air rises in the subsaturated atmosphere below the cloud, the absolute humidity stays constant, but RH increases as T decreases. The particles eventually deliquesce and keep taking up water.
- When the particles enter the cloud, which is supersaturated in H₂O they keep growing.
- S reaches a point higher than Scrit for the larger particle, which leads to activation of that particle.
- S always stays below S’crit for the smaller particle, so that one remains unactivated throughout the cloud. This is called the “interstitial” aerosol. Typically 10-50% of the particles activate and the rest remain as interstitial.
- Finally, if the air containing the particles goes beyond the top of the cloud, both particles lose most water because the air is again subsaturated.
- This animation was prepared by Don Collins at Texas A&M Univ.
Deliquescence and Efflorescence

From Don Collins, Texas A&M U.

### Deliquescence and Efflorescence

- **Dp / (Dp)dry**
- **RH (%)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>RHC (%)</th>
<th>RHD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>40</td>
<td>80</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>28</td>
<td>62</td>
</tr>
<tr>
<td>NaCl</td>
<td>42</td>
<td>75</td>
</tr>
</tbody>
</table>

From Don Collins, Texas A&M U.
From Don Collins, Texas A&M U.
From Don Collins, Texas A&M U.
From Don Collins, Texas A&M U.
The Many Aerosol Indirect Effects

Figure 2.10. Schematic diagram showing the various radiative mechanisms associated with cloud effects that have been identified as significant in relation to aerosols (modified from Haywood and Boucher, 2000). The small black dots represent aerosol particles, the larger open circles cloud droplets. Straight lines represent the incident and reflected solar radiation, and wavy lines represent terrestrial radiation. The filled white circles indicate cloud droplet number concentration (CDNC). The unperturbed cloud contains larger cloud drops as only natural aerosols are available as cloud condensation nuclei, while the perturbed cloud contains a greater number of smaller cloud drops as both natural and anthropogenic aerosols are available as cloud condensation nuclei (CCN). The vertical grey dashes represent rainfall, and LWC refers to the liquid water content.

From Don Collins, Texas A&M U.
The lifetime (& albedo) effect as proposed.

Q: is this a realistic model of the system?

Buffering in the System

- Lower precipitation leads to more evaporation @ cloud top
- Evap produces cooling, making environment more unstable
- Instability leads to deeper clouds and more rain!
Simulations of entire system

Biogeochemical Cycles

THE EARTH: ASSEMBLAGE OF ATOMS OF THE 92 NATURAL ELEMENTS

• Most abundant elements: oxygen (in solid earth!), iron (core), silicon (mantle), hydrogen (oceans), nitrogen, carbon, sulfur…

• The elemental composition of the Earth has remained essentially unchanged over its 4.5 Gyr history
  – Extraterrestrial inputs (e.g., from meteorites, cometary material) have been relatively unimportant
  – Escape to space has been restricted by gravity

• Biogeochemical cycling of these elements between the different reservoirs of the Earth system determines the composition of the Earth’s atmosphere and oceans, and the evolution of life
Biogeochemical Cycles II

Physical exchange, redox chemistry, biochemistry are involved

Q: where do atmospheric gases come from?
A. Captured by gravity from outside Earth
B. Formed by chemistry on the surface
C. Formed by chemistry on the ocean
D. Spewed by volcanoes
E. I don’t know

Surface reservoirs

Venus, Earth, and Mars

<table>
<thead>
<tr>
<th></th>
<th>Venus</th>
<th>Earth</th>
<th>Mars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (km)</td>
<td>6100</td>
<td>6400</td>
<td>3400</td>
</tr>
<tr>
<td>Surface pressure (atm)</td>
<td>91</td>
<td>1</td>
<td>0.007</td>
</tr>
<tr>
<td>CO₂ (mol/mol)</td>
<td>0.96</td>
<td>3x10⁻⁴</td>
<td>0.95</td>
</tr>
<tr>
<td>N₂ (mol/mol)</td>
<td>3.4x10⁻²</td>
<td>0.78</td>
<td>2.7x10⁻²</td>
</tr>
<tr>
<td>O₂ (mol/mol)</td>
<td>6.9x10⁻⁵</td>
<td>0.21</td>
<td>1.3x10⁻³</td>
</tr>
<tr>
<td>H₂O (mol/mol)</td>
<td>3x10⁻³</td>
<td>1x10⁻²</td>
<td>3x10⁻⁴</td>
</tr>
</tbody>
</table>
Runaway Greenhouse Effect on Venus

due to accumulation of water vapor from volcanic outgassing early in its history

...did not happen on Earth because farther from Sun; as water accumulated it reached saturation and precipitated, forming the oceans

History of Earth’s Atmosphere

Q: what caused life to move into continents around 0.4 Gy BP?
**Q:** How come O₃ increased faster than O₂?

- Chapman Cycle in the stratosphere:
  
  \[
  \begin{align*}
  O_2 + h\nu & \rightarrow 2 \cdot O \\
  O\cdot + O_2 & \rightarrow O_3 \\
  O_3 + h\nu & \rightarrow O_2 + O \\
  O_3 + O\cdot & \rightarrow 2 O_2
  \end{align*}
  \]
Material Supply for Life

A small acorn over time can grow into a huge oak tree. The tree can weigh many tons. Where does most of the mass come from as the tree grows?

A) Minerals in the soil  
B) Organic matter in the soil  
C) Gases in the air  
D) Sunlight  
E) I don’t know

---

Fast O Cycle: biosphere-atmosphere

- Source of $O_2$: photosynthesis
  
  $nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2$

- Sink: respiration/decay
  
  $(CH_2O)_n + nO_2 \rightarrow nCO_2 + nH_2O$

$O_2$ lifetime: 5000 years
...however, abundance of organic carbon in biosphere/soil/ocean reservoirs is too small to control atmospheric O$_2$ levels

From Jacob

Slow O Cycle: Atmosphere-Lithosphere

From Jacob
Uptake of CO₂ by Oceans

\[
\begin{align*}
\text{CO}_2(g) & \quad \text{OCEAN} \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \\
\text{K}_1 & = 9 \times 10^{-7} \text{ M} & \text{K}_1 & = 9 \times 10^{-7} \text{ M} \\
\text{K}_2 & = 7 \times 10^{-10} \text{ M} & \text{K}_2 & = 7 \times 10^{-10} \text{ M} \\
\end{align*}
\]

\[\text{KH} = 3 \times 10^{-2} \text{ M atm}^{-1}\]

From Jacob

CFC-11 in the Atlantic

1 JUNE 2006

Fig. 1. CFC-11 from the NA09 section along 20°W taken in August 1993: (a) Observations, (b) ocean-alone Oen run, (c) mean of the ESh, ESh, and ESh runs, and (d) column inventory of CFC-11 in moles km⁻² along the section from observations (crosses), Oen run (squares), and the range of the ESh, ESh, and ESh runs (shading).
Observed uptake of fossil fuel CO$_2$ by the oceans

Source: Robert Key, Princeton Univ, SciAm March 2006

compare to ~300 μmoles CO$_2$"
Human Influence on C Cycle

Natural fluxes in black; anthropogenic contribution (1990s) in red

From IPCC 2007 via Jacob

EVIDENCE FOR LAND UPTAKE OF CO₂ FROM TRENDS IN O₂, 1990-2000

From Jacob
QUESTIONS

1. Melting of polar icecaps would reduce deep water formation and hence the transfer of \( CO_2 \) to the deep ocean. Why?

2. It is proposed to reduce greenhouse emissions by asking farmers to compost rather than burn their agricultural waste. Does this make sense?

3. From the standpoint of controlling atmospheric \( CO_2 \), is it better to heat your home with a wood stove or by natural gas?

4. The conventional scientific view is that fossil fuel \( CO_2 \) injected to the atmosphere will affect the atmosphere for \( \approx 100 \) years before transfer to the deep ocean and that it represents therefore a long-term environmental problem. This view has been challenged by skeptics on the basis of bomb \( ^{14}CO_2 \) data. Above-ground nuclear tests in the 1950s injected large amounts of \( ^{14}CO_2 \) in the atmosphere, but atmospheric observations following the nuclear test ban in 1962 showed an exponential decay of \( ^{14}CO_2 \) back to background values on a time scale of 5 years. This shows, according to skeptics, that if we were to shut down fossil fuel emissions then \( CO_2 \) would return to natural background values within 5 years. What do you think of this reasoning?

5. You wish to fly from Boston to California on a commercial flight that consumes 100,000 lbs of jet fuel for the trip. The company offers - as an extra charge on your ticket - to make your personal trip carbon-neutral by planting trees. Does this seem practical, in terms of the number of trees that would need to be planted? And is this a reasonable long-term proposition for mitigating your personal carbon footprint?