# 12.842 / 12.301 Past and Present Climate

Fall 2008

# 12.842
# Climate Physics and Chemistry
# Fall 2008

## Natural and Fossil Fuel $CO_2$ in the Ocean I

# Reading assignment:

Sarmiento and Gruber, Physics Today, Aug. 30, 2002

# Some useful URLs:

www.ngdc.noaa.gov

cdiac.esd.ornl.gov/trends/trends.htm

http://www.ldeo.columbia.edu/res/pi/CO2/

http://www.grida.no/CLIMATE/IPCC_TAR/WG1/index.htm

# Ocean and Atmospheric Chemistry

## Goals for this part of the subject (I)

- *The Global Carbon System:*
  - *Inform the class of relevant facts and figures concerning fossil fuel $CO_2$ emissions and their fate so as to be able to think and act in science and public discourse*
  - *Understand the basic processes that govern movements of $CO_2$ in the earth surface environment*
  - *Develop an understanding of how these processes are incorporated into models that predict future atmospheric carbon dioxide levels*

# Ocean and Atmospheric Chemistry

## Goals for this part of the subject (II)

- *Atmospheric Chemistry:*
  - *Develop an understanding of gas phase reactions in the atmosphere*
  - *Understand the sources and sinks of CH4, N2O, and CFCs*
  - *Evaluate the past and future evolution of these gases*

# Direct measurements of $CO_2$ in the atmosphere for the past 47 years

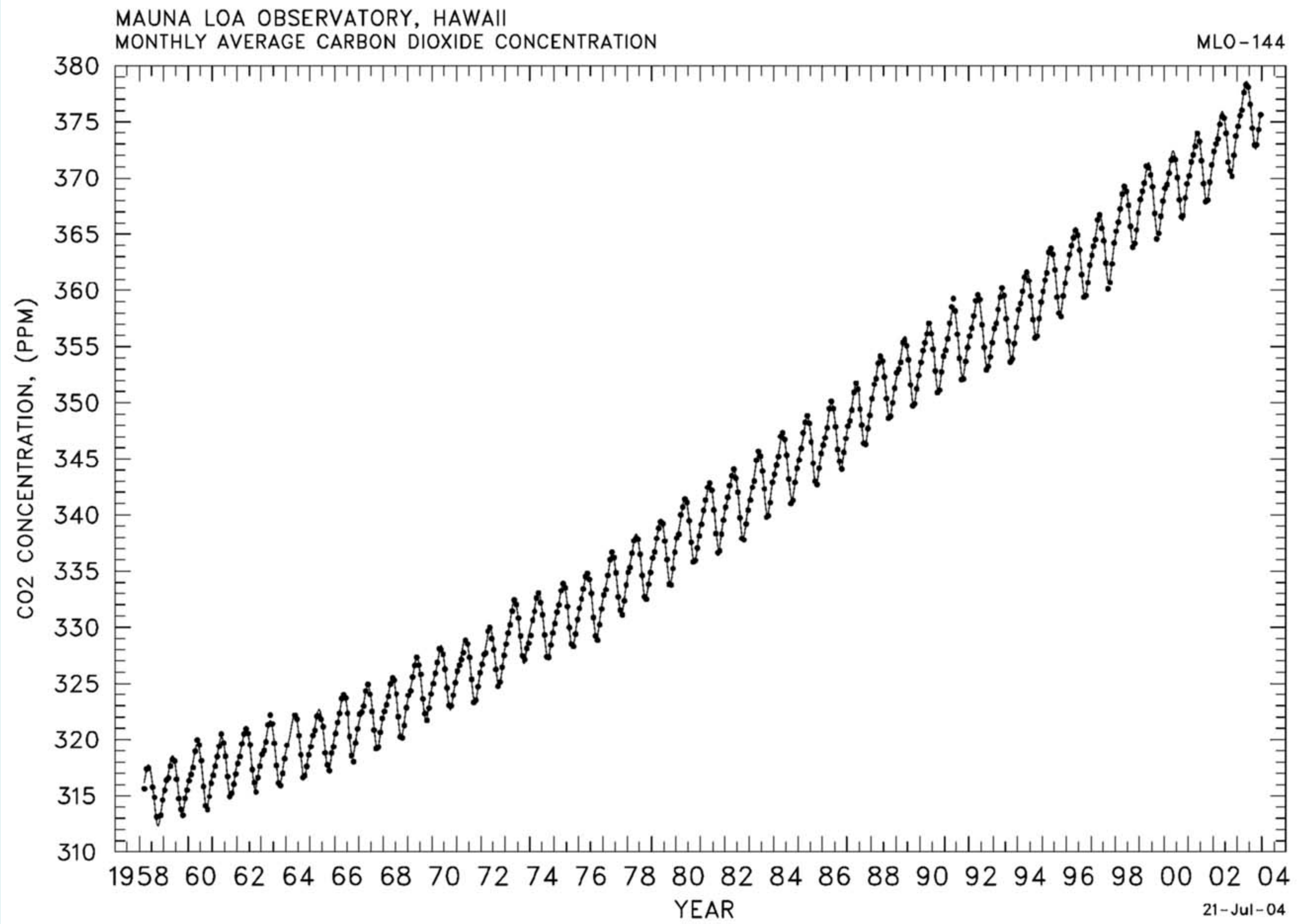
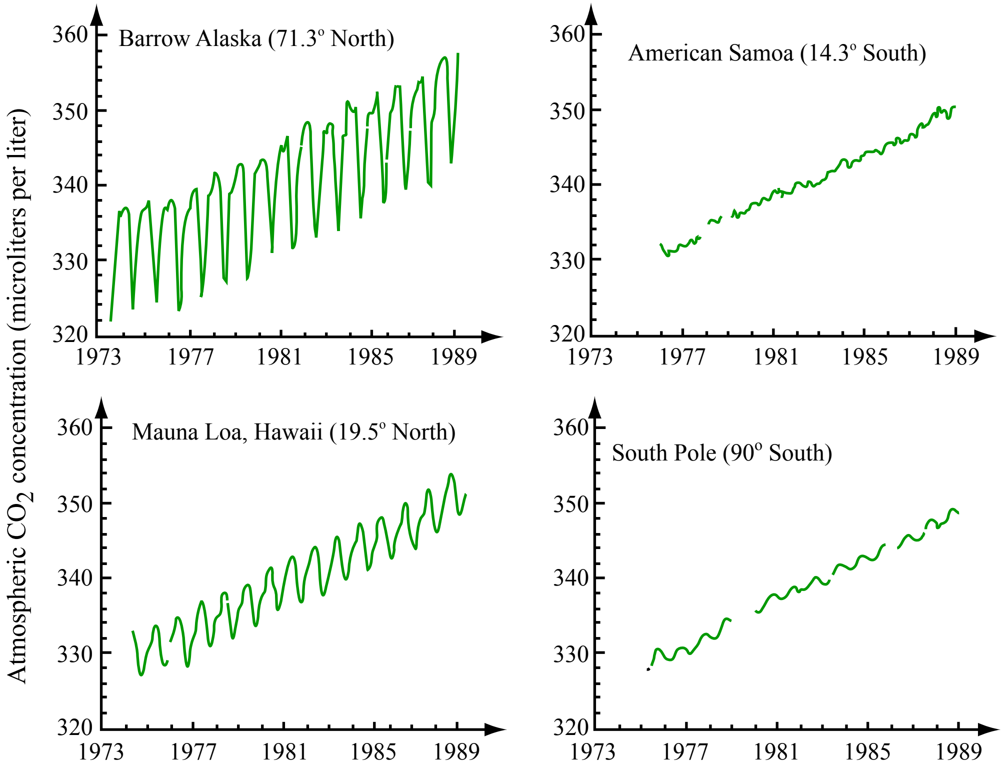


Image courtesy of DOE.

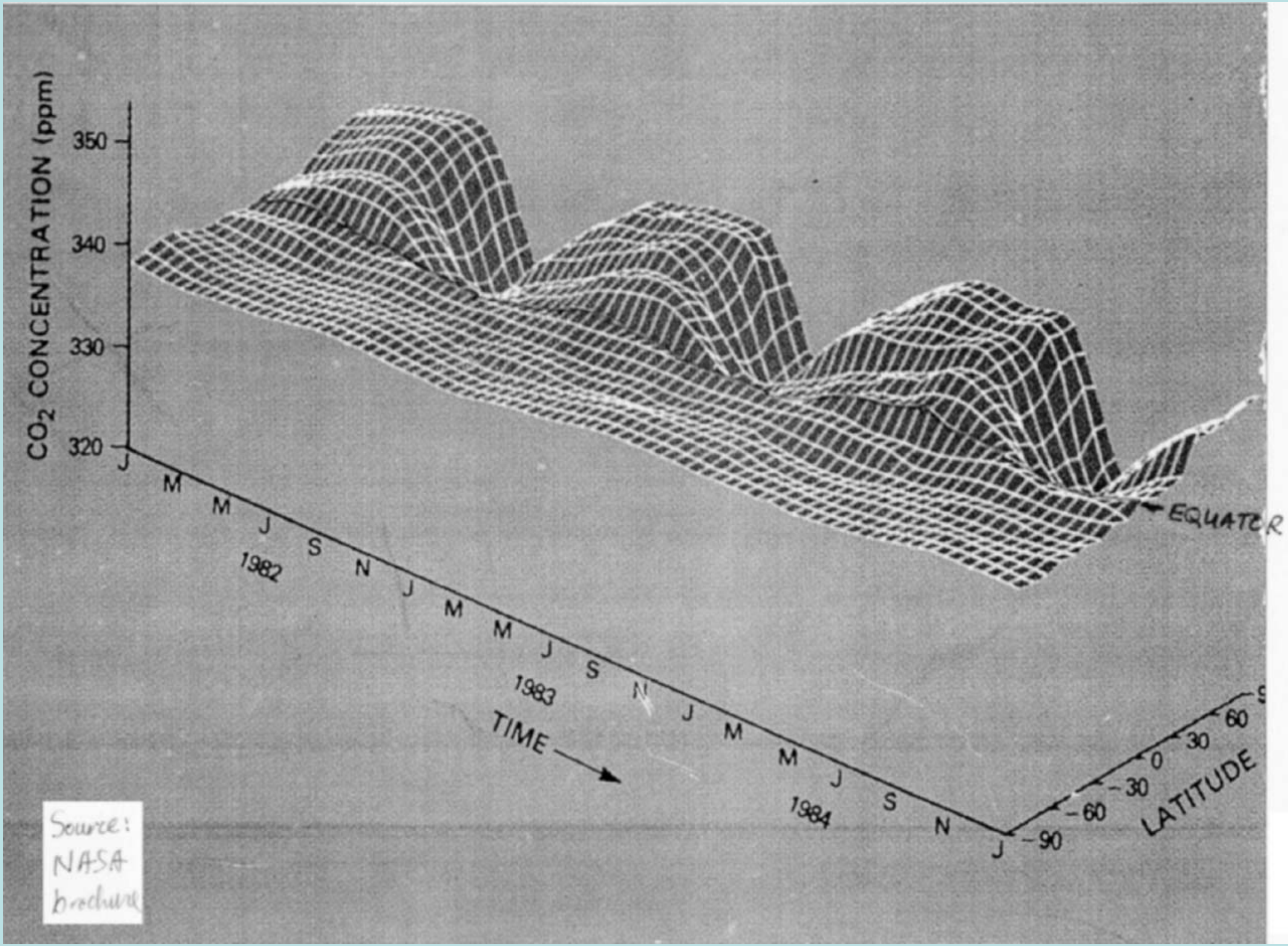
# Spatial variability of atmospheric CO$_2$



Seasonal cycles of atmospheric CO$_2$ concentrations are illustrated by measurements from four monitoring stations where the National Oceanic and Atmospheric Administration takes continuous readings. Analysis of the measurements shows that seasonal cycles in the Northern Hemisphere-which reflect the dominance of photosynthesis in the summer and plant respiration in the winter-seem to be increasing in amplitude. This may be a result of global warming. The dots represent monthly averages. The data are from Peterson et al. 1986; Komhyr et al. 1989; Thoning, Tans and Komhyr 1989; Waterman et al. 1989; and Gillette et al. 1987.

Figure by MIT OpenCourseWare.

# Atmospheric $CO_2$ vs. latitude and time



Source: NASA brochur

Image courtesy of NASA.

“And in my judgment, we need to set aside whether or not greenhouse gases have been caused by mankind or because of natural effects, …”

George W. Bush
Chicago, May 22, 2006

# Global $CO_2$ emissions from fossil-fuel burning, cement production, and gas flaring

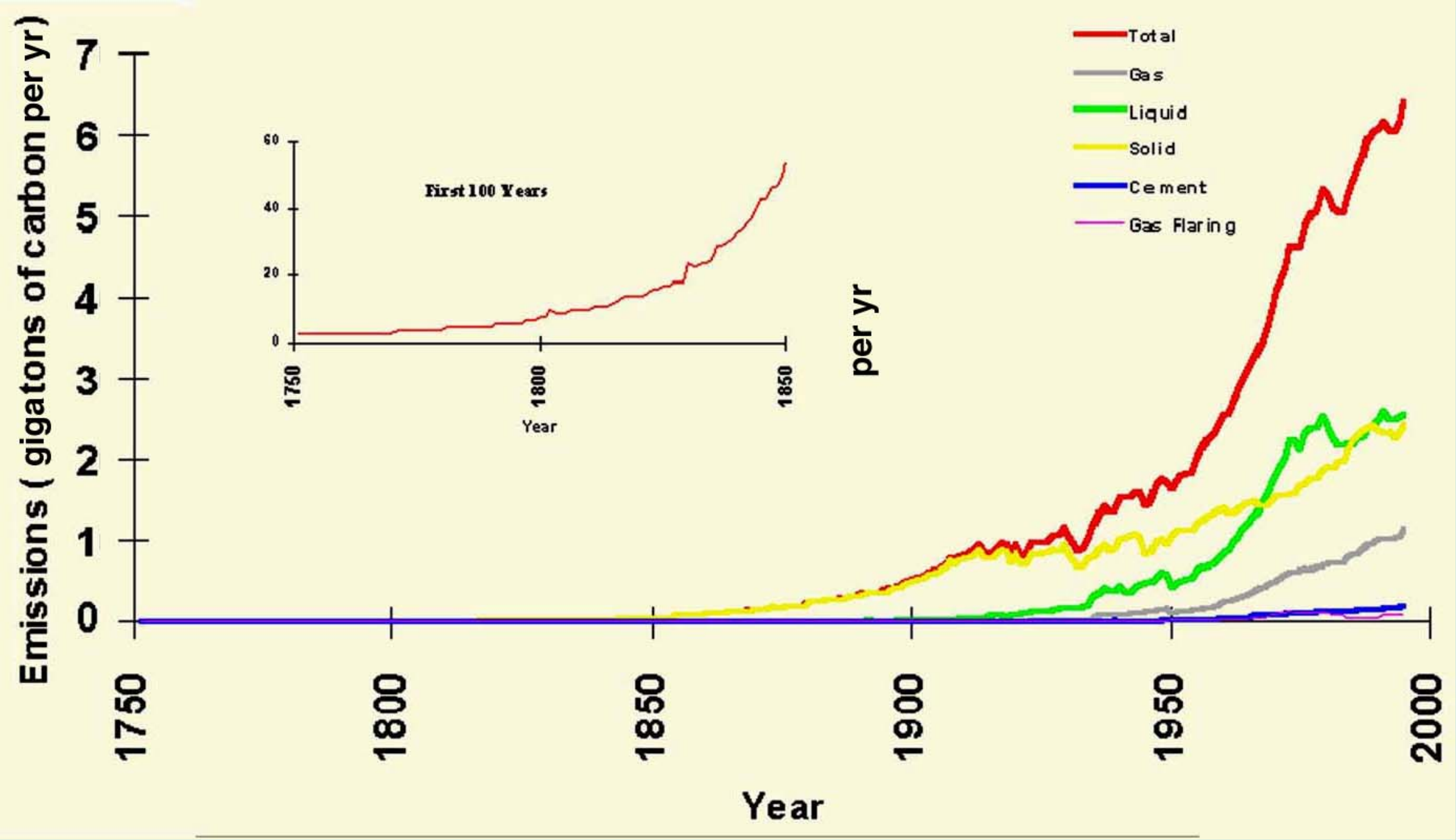
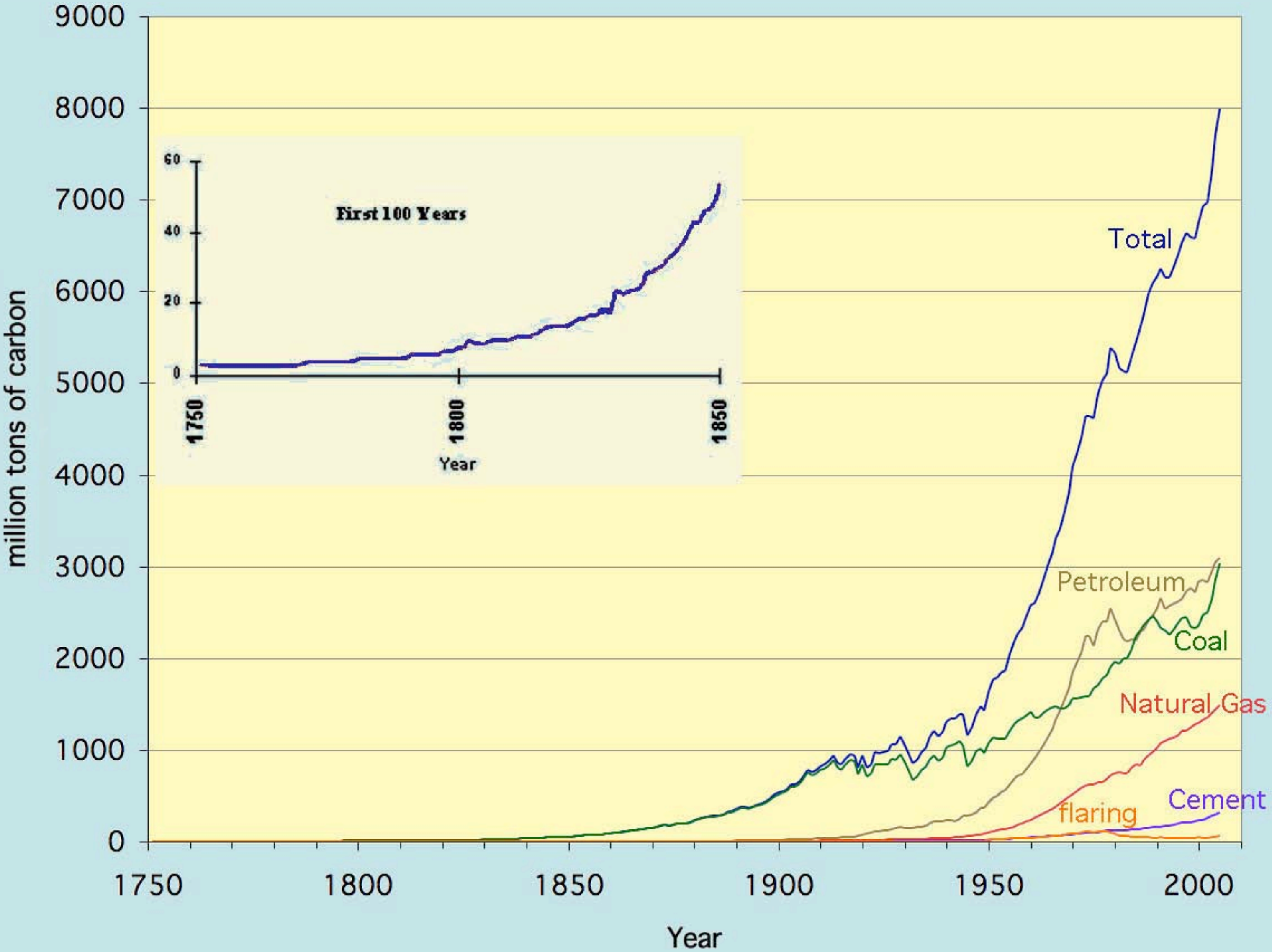
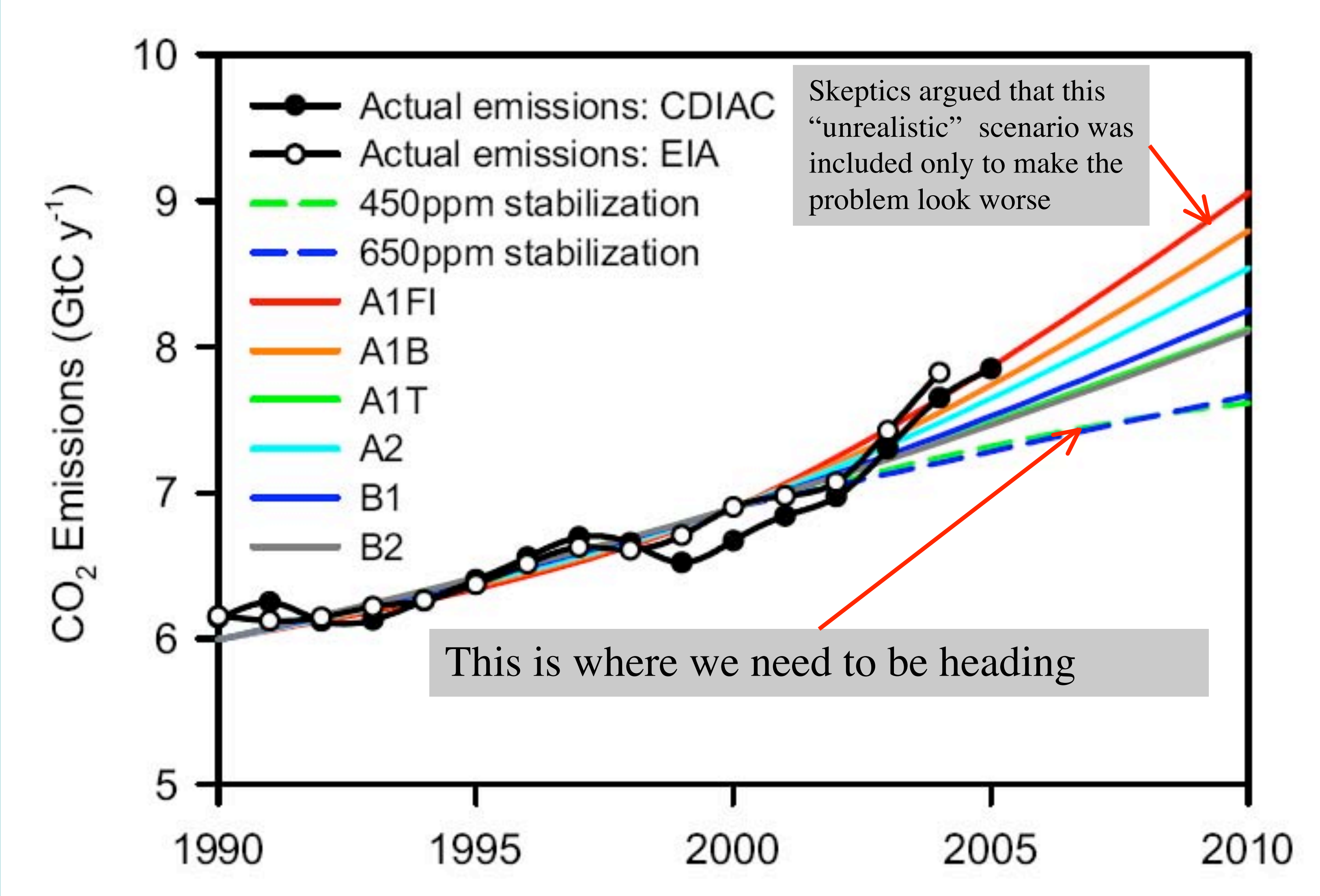


Image courtesy of DOE.

# Anthropogenic $CO_2$ emissions through 2005



# Emissions are rising faster than expected



Skeptics argued that this "unrealistic" scenario was included only to make the problem look worse

This is where we need to be heading

Figure courtesy of David Keith. Used with permission.

# Global Oil Production

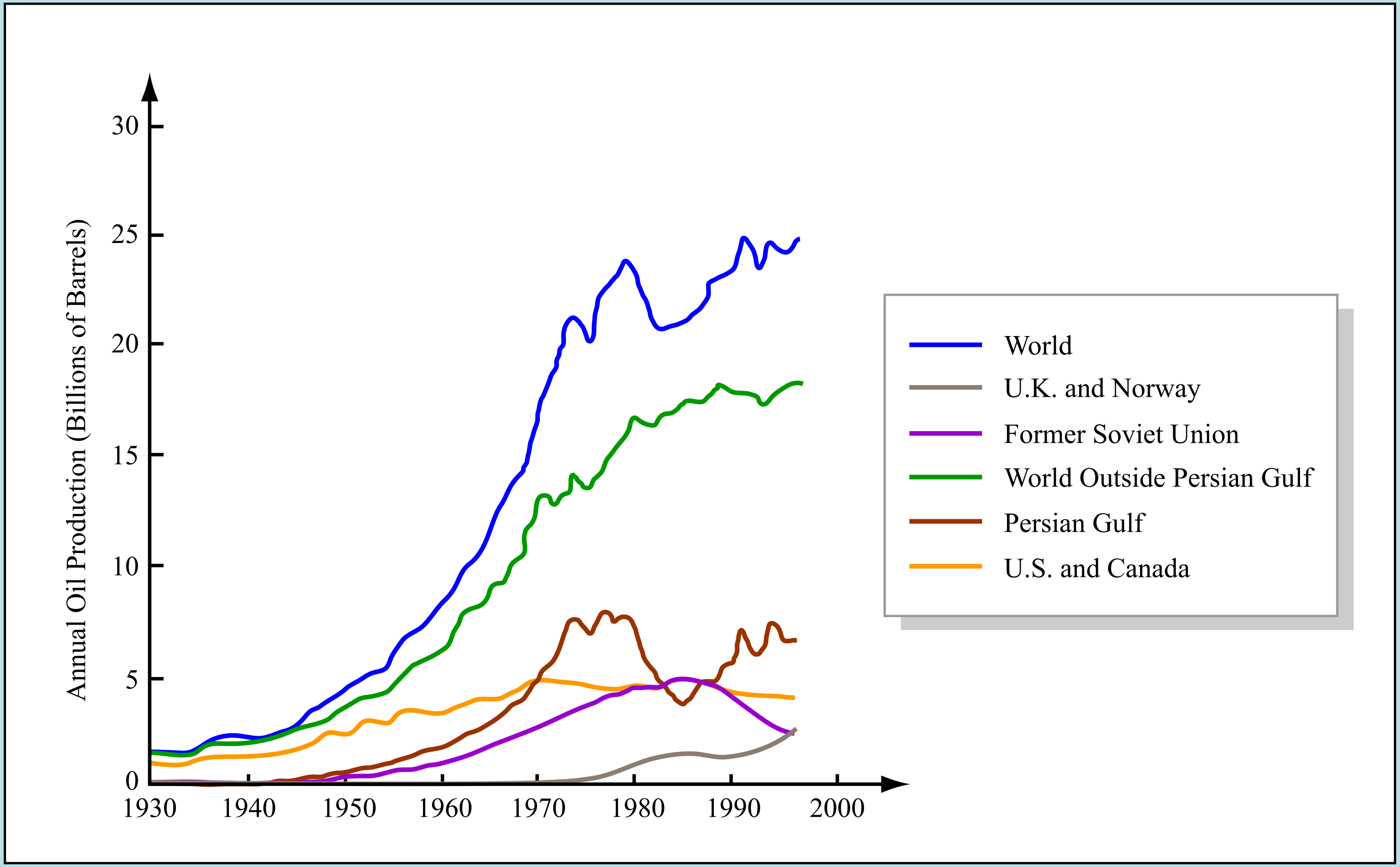
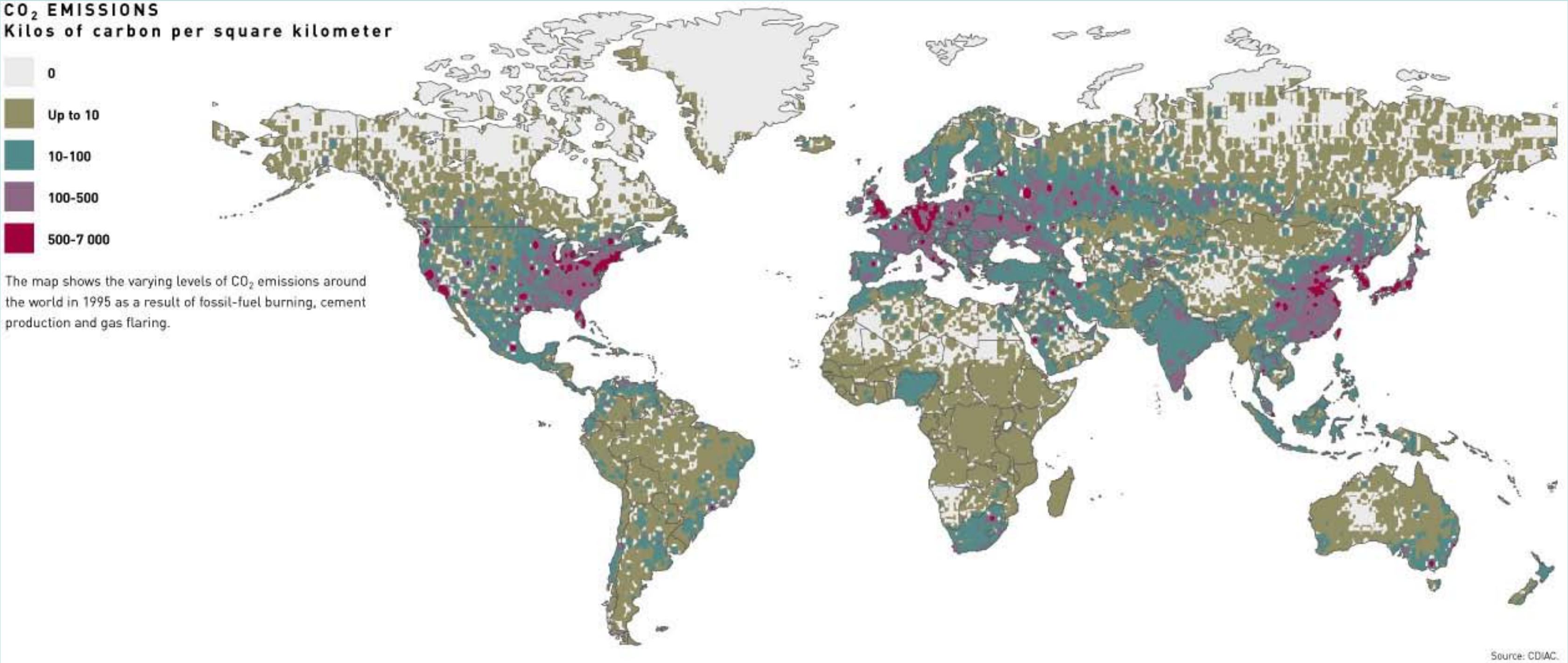


Figure by MIT OpenCourseWare.

# Global $CO_2$ emissions by area:



The map shows the varying levels of $CO_2$ emissions around the world in 1995 as a result of fossil-fuel burning, cement production and gas flaring.

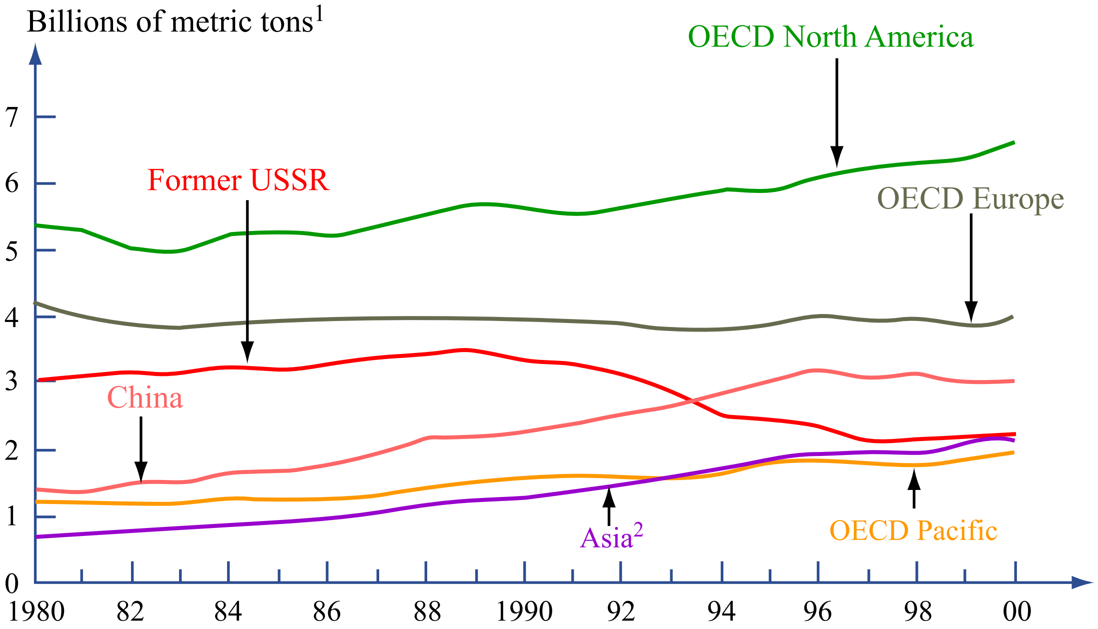
Source: CDIAC.

Image courtesy of DOE.

# $CO_2$ emissions by region:

## GREENHOUSE GAS

$CO_2$ emissions from Europe have stabilized, but those from North America have risen sharply



1. Emissions from fuel combustion only
2. Excluding China. OECD = Organization for Economic Cooperation & Development

Source: C&EN Dec. 16, 2002

Figure by MIT OpenCourseWare.

# Direct measurements of $CO_2$ in the atmosphere for the past 47 years

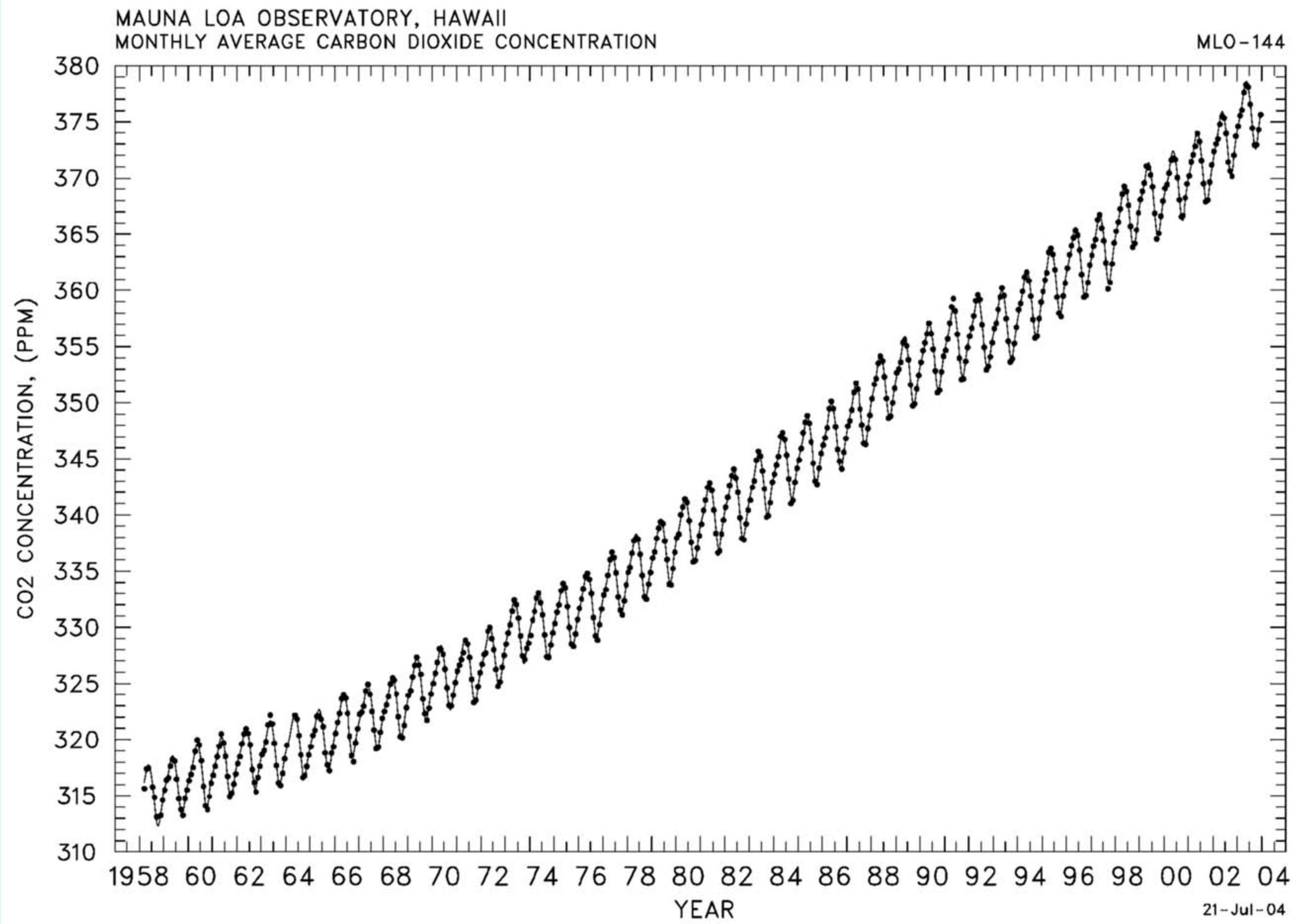
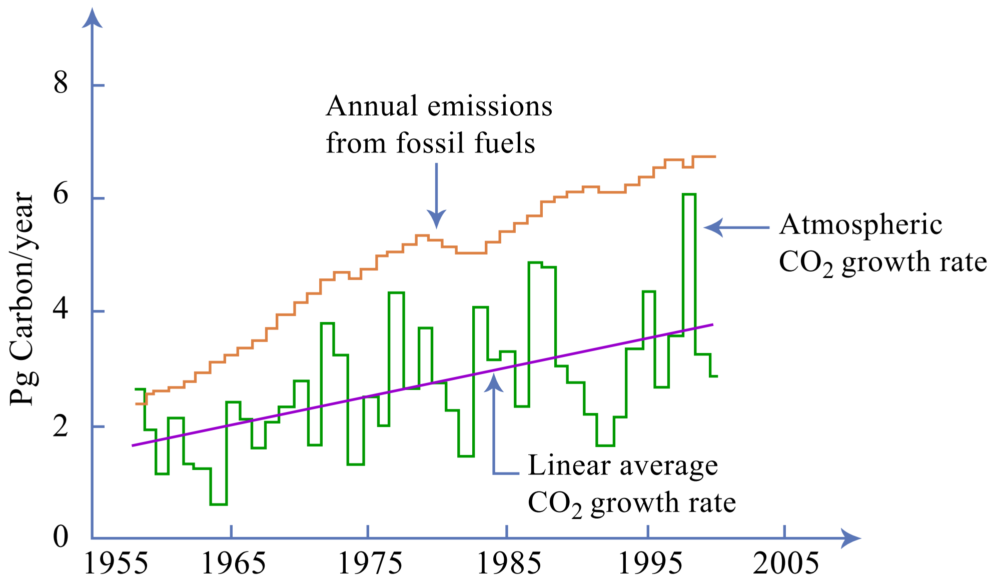


Image courtesy of DOE.

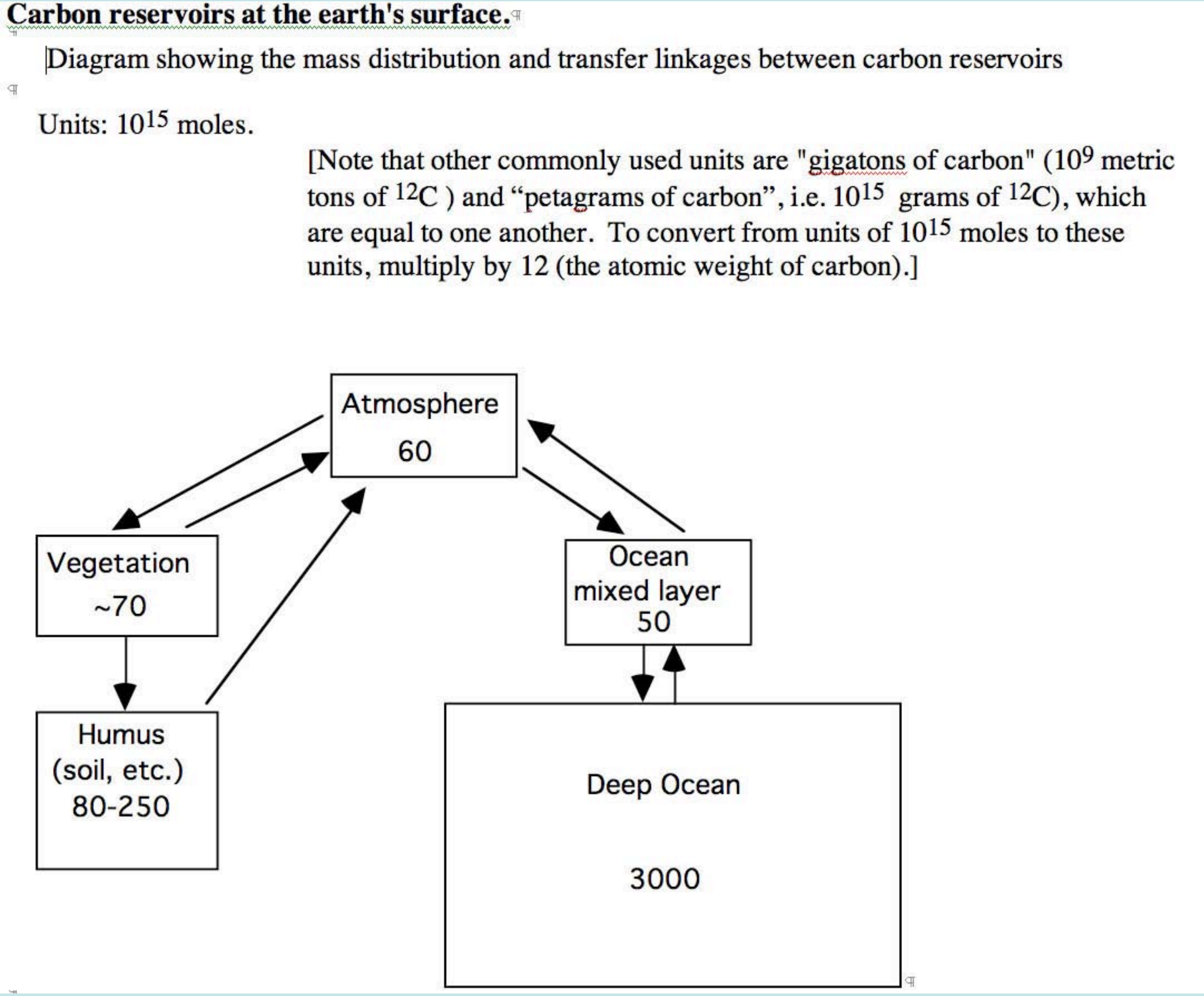
# Atmospheric $CO_2$ growth rate



**Going up**. Annual global rates of $CO_2$ accumulation in the atmosphere and $CO_2$ emission from fossil fuel burning since 1958.

Figure by MIT OpenCourseWare based on *Science* 298: 2344.

# Carbon reservoirs



**Carbon reservoirs at the earth's surface.**

Diagram showing the mass distribution and transfer linkages between carbon reservoirs

Units: $10^{15}$ moles.

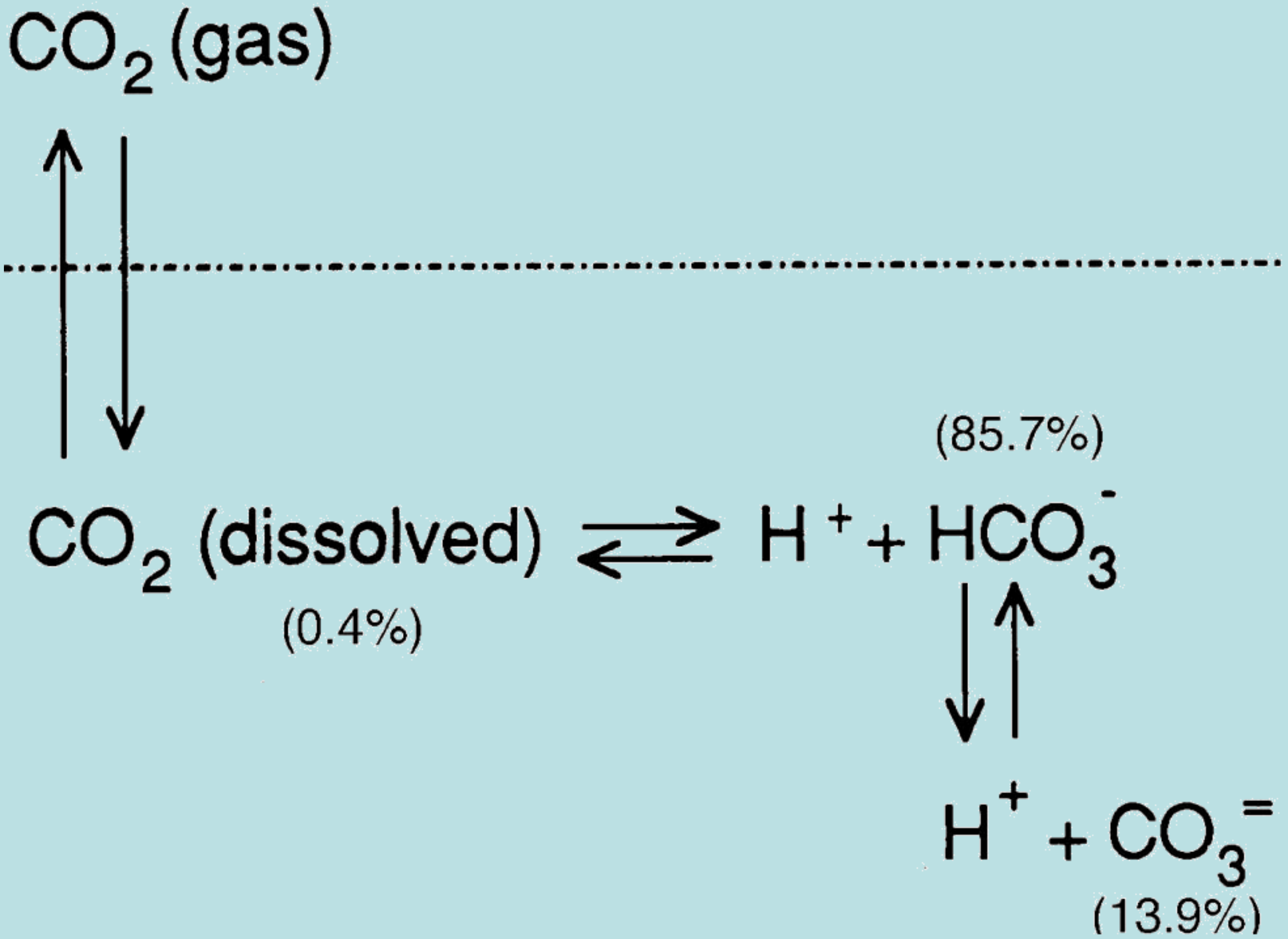
[Note that other commonly used units are "gigatons of carbon" ($10^9$ metric tons of $^{12}C$ ) and “petagrams of carbon”, i.e. $10^{15}$ grams of $^{12}C$), which are equal to one another. To convert from units of $10^{15}$ moles to these units, multiply by 12 (the atomic weight of carbon).]

Image removed due to copyright restrictions.

Citation: Figure 1. Sarmiento J. L., and N. Gruber. *Physics Today* (August 2002): 30-36.

# The Revelle Factor

Revelle Factor $$R = \frac{\Delta p_{CO2} / p_{CO2}}{\Delta \Sigma CO_2 / \Sigma CO_2} \sim 10$$



$CO_2$ (gas)

$CO_2$ (dissolved) $\rightleftharpoons$ $H^+ + HCO_3^-$

(0.4%)

(85.7%)

$H^+ + CO_3^=$

(13.9%)

# Ocean uptake of fossil fuel $CO_2$: two limiting cases and the real situation

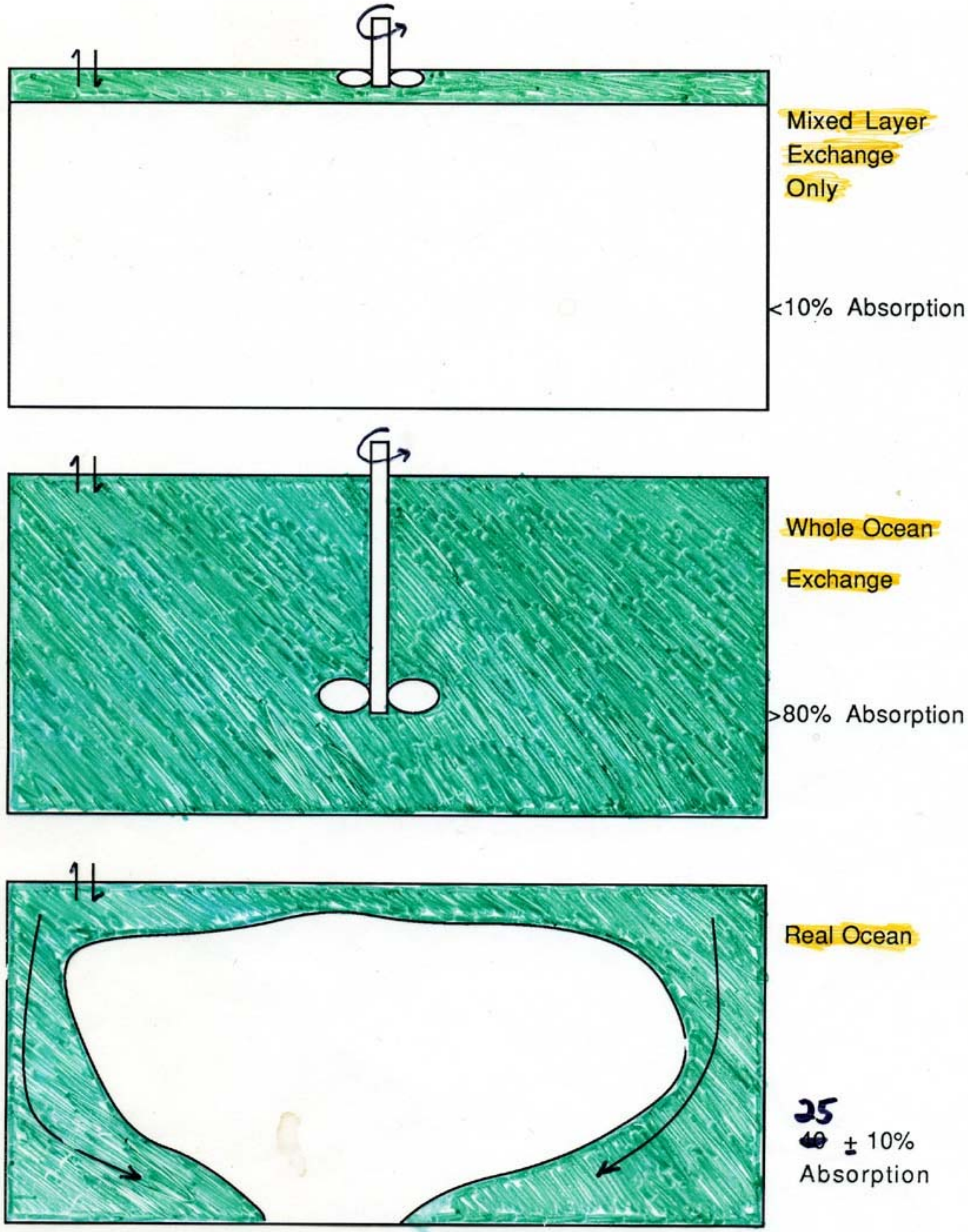


Image removed due to copyright restrictions.
Citation: Figure 1-1. Broecker, W. S., and T. H. Peng.
*Tracers in the Sea*. Eldigio Press Lamont Doherty
Geological Observatory, 1982, 690 pages.

Image removed due to copyright restrictions.
Citation: Figure 1-2. Broecker, W. S., and T. H. Peng.
*Tracers in the Sea*. Eldigio Press Lamont Doherty
Geological Observatory, 1982, 690 pages.

# Fossil fuel $CO_2$ absorption by the ocean: how much, how fast?

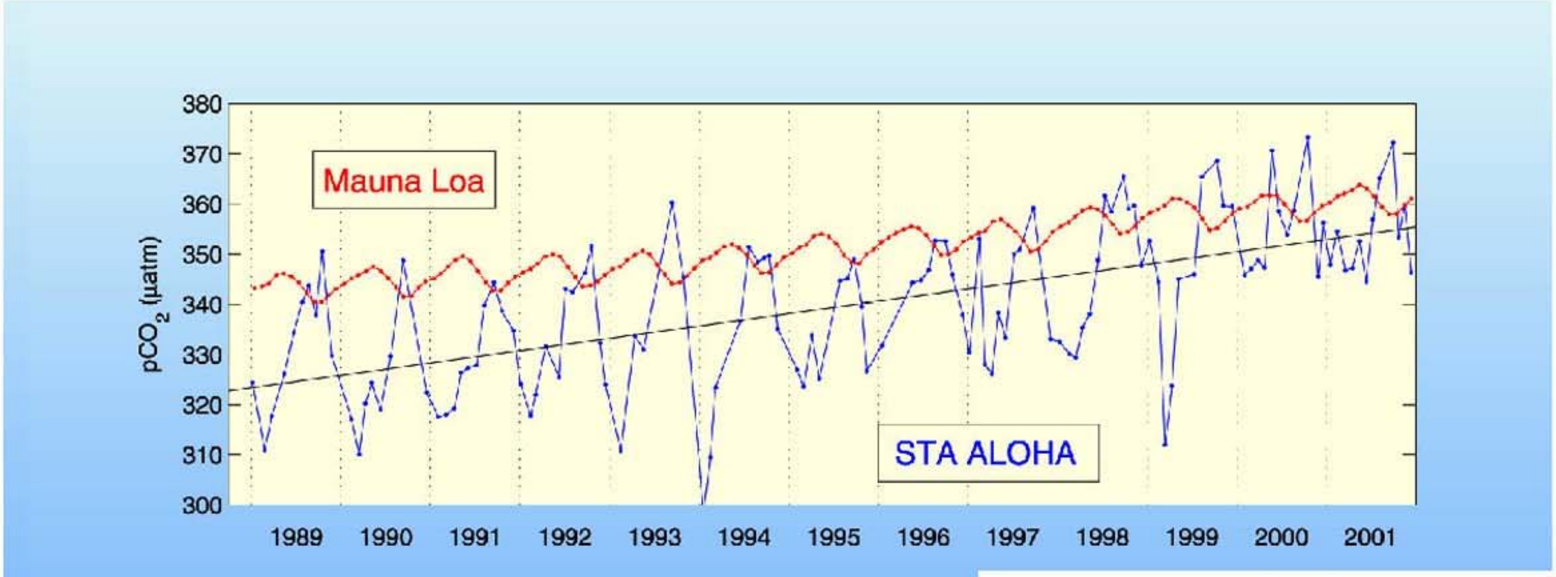
How fast does the ocean absorb $CO_2$? What are the important rate- and capacity-limiting processes? How might these processes change in the future?

- Direct observation of changing ocean $CO_2$ concentrations ("the oceanic Keeling Curve"): this method is difficult because the ocean response is 10% of the atmospheric forcing. The $CO_2$ content of the atmosphere has increased by 20% over the past 45 years, so ocean water in equilibrium with the atmosphere has only increased by 2%. And most of the absorbed $CO_2$ has been mixed into a large pre-existing background in the deep ocean, so the signal is much less than 2%.

- Estimation by subtracting out the natural background, based on "Redfield Ratio" stochiometry. This method relies on the higher accuracy of recent measurements and the stoichiometry of the oxidation of marine organic matter. Works reasonably well for North Atlantic, more difficult for Southern Ocean and Pacific (higher background, less certain initial conditions).

- Tracer method, combined with simple robust models: tracers such as bomb tritium and chlorofluorocarbons enter the ocean from the atmospere, much as does $CO_2$. We can safely assume that water that has tritium and CFCs also has anthropogenic $CO_2$. The method requires some correction for the chemical differences between these tracers and for the different time histories of emissions. Nonetheless, these corrections are straightforward and the model-dependence is not strong.

# Change of $pCO_2$ at the ocean surface at the JGOFS station HOT over the 13 years period, 1989 -2002

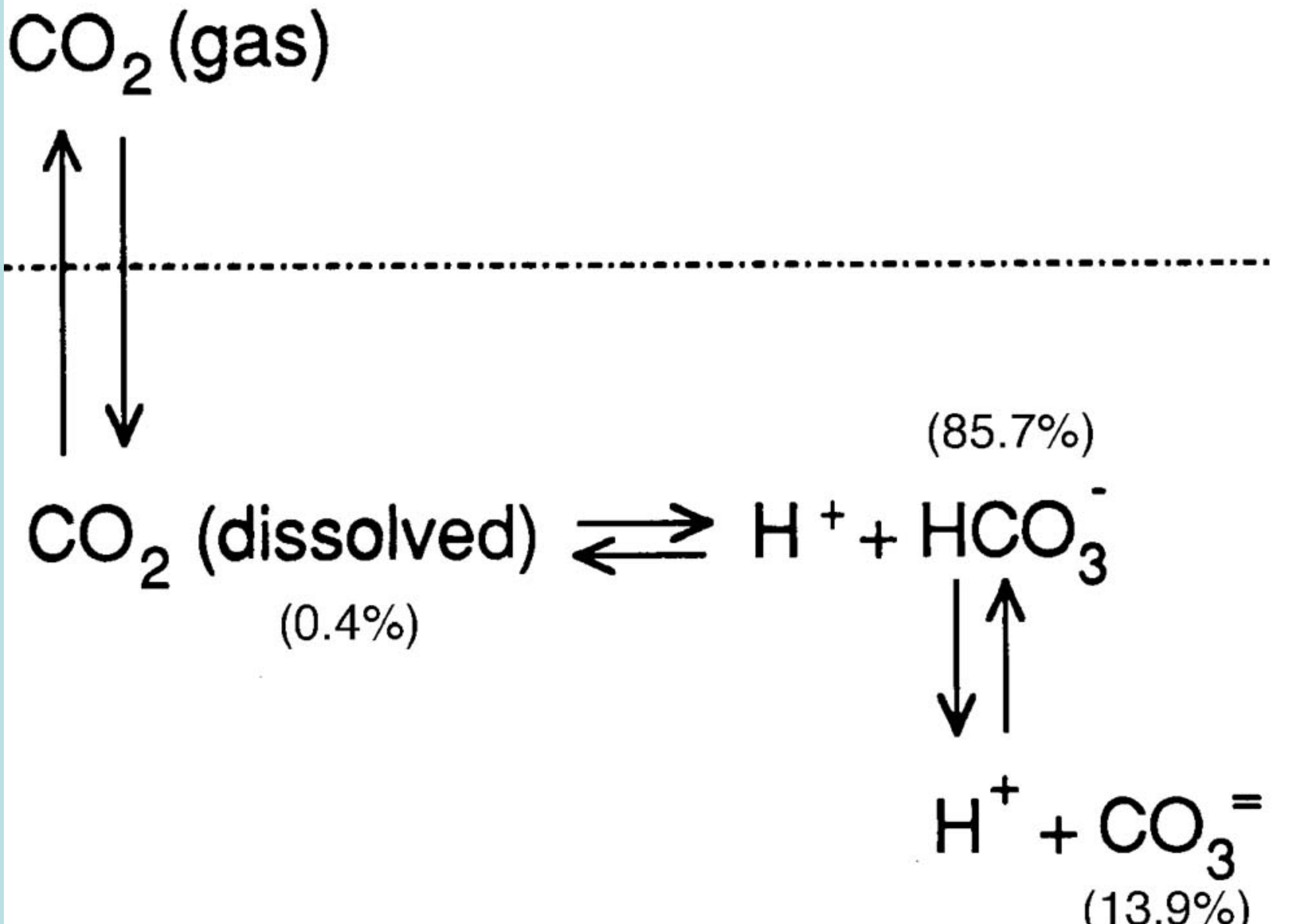


D.Karl,JGOFS Ocean Science Conference
Washington DC, May 2003

Courtesy of David Karl, University of Hawaii at Manoa. Used with permission.

# The Revelle Factor

Revelle Factor $R = \frac{\Delta p_{CO2} / p_{CO2}}{\Delta \Sigma CO_2 / \Sigma CO_2} \sim 10$



# Outline:

- Seawater $CO_2$ thermodynamics
- Estimating gas exchange rates
  - Thin film model
  - Piston velocity
  - Wind speed dependence
- Ocean $CO_2$ exchange
  - Global $CO_2$ exchange rate
  - Air-sea disequilibrium and spatial variability
- Estimating the penetration of ocean surface waters into the deep ocean
  - Ocean circulation primer
  - Transient tracers
- Estimating ocean uptake of fossil fuel $CO_2$: is there a "missing sink"?
- The $\Delta O_2/\Delta CO_2$ method for estimating ocean and biospheric fossil fuel uptake: quantifying the "missing sink"
- Other methods for observing fossil fuel $CO_2$ uptake
  - $\delta^{13}C$
  - "excess $CO_2$"
  - Historical proxy methods: $\delta^{13}C$ in tree rings and corals
- Extrapolating fossil fuel into the future

# Physical chemistry of $CO_2$ in the ocean 1

A. Two useful conservative quantities (properties that mix linearly) are:

$\Sigma CO_2 = [CO_2(aq)] + [HCO_3^-] + [CO_3^=]$ *(total dissolved inorganic carbon, DIC)*

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^=]$$
$$+ [B(OH)_4^-] + [OH^-] - [H^+]$$
$$+ (\text{etc...})$$

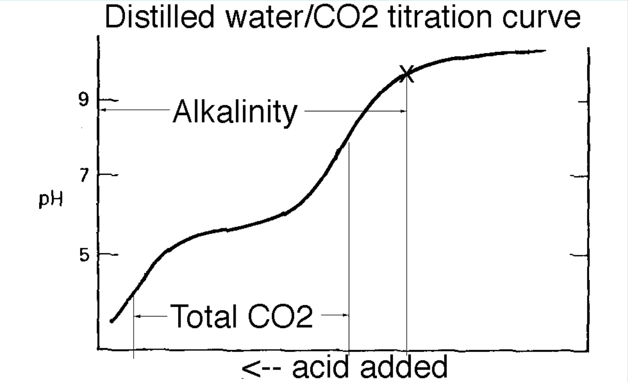
"Alkalinity" is a re-arranged charge balance equation which divides ions into those that have acid-base reactions and those that don't:

e.g., in a system consisting of a solution of NaCl, $MgSO_4$, $NaCO_3$, and $NaHCO_3$:

$$[Na^+] + 2[Mg^{++}] - 2[SO_4^=] = [HCO_3^-] + 2[CO_3^=] + [OH^-] - [H^+]$$
$$= \text{Alkalinity}$$

Adding or removing $CO_2$ from a water sample does not change the alkalinity (convince yourself of this!)

# Operationally in marine chemistry, alkalinity is defined as the number of equivalents of acid needed to bring a sample to the $CO_2$ endpoint:



# Physical chemistry of $CO_2$ in the ocean

"Apparent" thermodynamic constants: because seawater is a "high ionic strength" solution (i.e., it is very salty), conventional thermodynamic constants (activity coefficients, etc.) are difficult to define because of strong ionic interactions. But because the composition of seawater (for major ions) is constant save for variations in total salt content, we can adopt "apparent constants" which incorporate the activity coefficients and ion interactions into the constant (denoted by '):

i. $CO_2\ (gas) = CO_2\ (aq)$ $\qquad \alpha_s' = \dfrac{[CO_2(aq)]}{pCO_2} \approx 10^{-1.5}$

ii. $CO_2(aq) + H_2O = H^+ + HCO_3^-$ $\qquad K_1' = \dfrac{[H^+][HCO_3^-]}{[CO_2(aq)]} \approx 10^{-6.0}$

iii. $HCO_3^- = H^+ + CO_3^=$ $\qquad K_2' = \dfrac{[H^+][CO_3^=]}{[HCO_3^-]} \approx 10^{-9.1}$

iv. $B(OH)_3 + H_2O = B(OH)_4^- + H^+$ $\qquad K_B' = \dfrac{[H^+]\ [B(OH)_4^-]}{[B(OH)_3]} \approx 10^{-8.7}$

These "apparent constants" are functions of temperature, salinity, and pressure.

*Variables:*

$pCO_2$

$[CO_2(aq)]$

$[HCO_3^-]$

$[CO_3^=]$

$[B(OH)_3]$

$[B(OH)_4^-]$

$[H^+]$

T

S

---

9 variables

*Knowns:*

4 equations

T

S

$\Sigma B$ / S

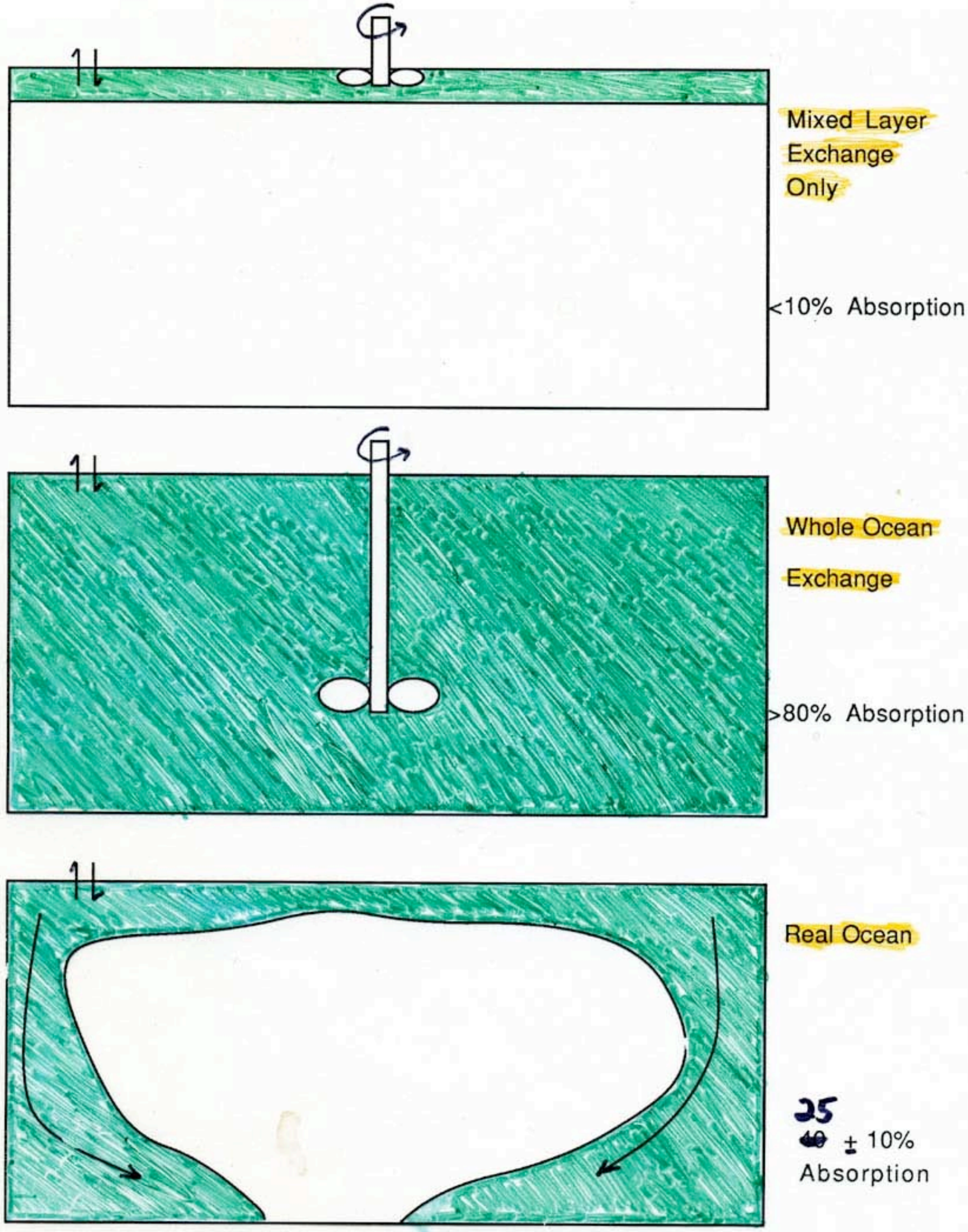
2 specified parameters

(e.g. Alk, $\Sigma CO_2$)

---

9 equations or specified

# Ocean uptake of fossil fuel $CO_2$: two limiting cases and the real situation



# Equilibrium uptake of fossil fuel $CO_2$

- Using the Revelle Factor, we can explore the consequences when equilibrium between the ocean and atmosphere is attained, given hypothetical changes in $p_{CO2}$:

| **Atmosphere($10^{15}$moles)** | **Mixed Layer** | **Whole Ocean** |
|---|---|---|
| **60** | **50** | **3050** |
| **66** | **50.5** | **3080** |

- a. **This result indicates that:**
- **(1) The mixed layer on its own can't take up very much fossil fuel $CO_2$,** and
- **(2) The whole ocean would take up ~80% at equilibrium.**
- In other words, an equilibrium model cannot account for the 50% uptake ratio. It seems that uptake might have been much more or much less than it has, depending on the extent to which the deep ocean equilibrates.

- b. So we need to know what controls the uptake of $CO_2$ by the deep ocean.

# Fundamental factors controlling ocean fossil fuel $CO_2$ uptake

- Physical transfers:
  - $CO_2$ crosses the air-sea interface
    - Chemical equilibrium determines total possible transfer

      (carbonic acid equilibrium constants, summarized by Revelle Factor)
    - Gas exchange dynamics across the air-sea interface determines the rate of approach to chemical equilibrium. Gas exchange is a function of wind speed and other factors.
      - Estimated from natural $^{14}C$ uptake, $^{222}Rn$ deficit, and tracer release experiments
  - $CO_2$ that dissolves into the surface mixed layer is carried by ocean circulation into the upper ocean and deep sea.
    - How fast does this occur, and what factors affect the rate of circulation?

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# Basic Gas Exchange

- With one exception to be mentioned later, gas exchange should drive the a system that is out of equilibrium towards one that is in equilibrium.
- At equilibrium, gas solubility is proportional to the partial pressure of the gas:
  - e.g.

$$\alpha_s' = \frac{[CO_2(aq)]}{pCO_2}$$

- Hence when a gas is out of equilibrium we expect the net flux of the gas our of a fixed surface area to be proportional to the departure from equilibrium, when everything else is constant:

$$\textbf{Flux} = \textbf{constant} * [C_{\textbf{equilibrium}} - C]$$

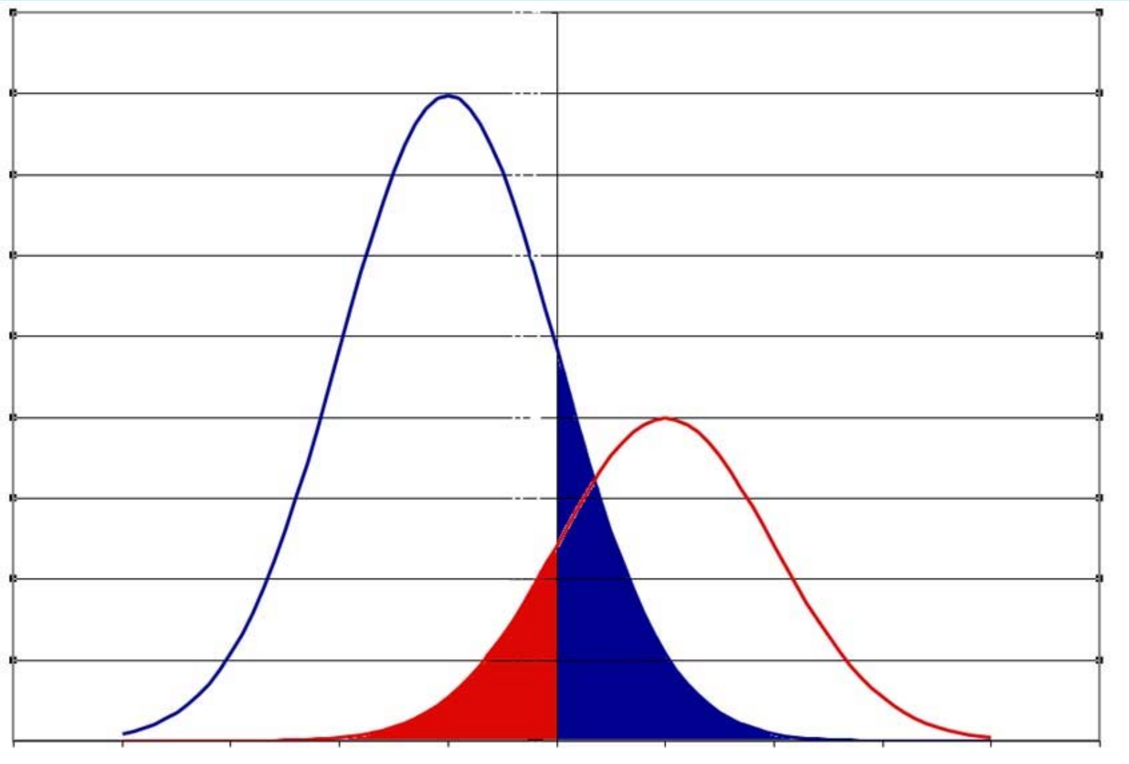
mol $cm^{-2}$ $sec^{-1}$ cm $sec^{-1}$ mol $cm^{-3}$

- The proportionality constant, with dimensions of velocity, can be considered as a “gas exchange coefficient”. What it means physically, and what it depends on, is a function of the gas exchange model.
  -

# Stagnant Film Model of Gas Exchange

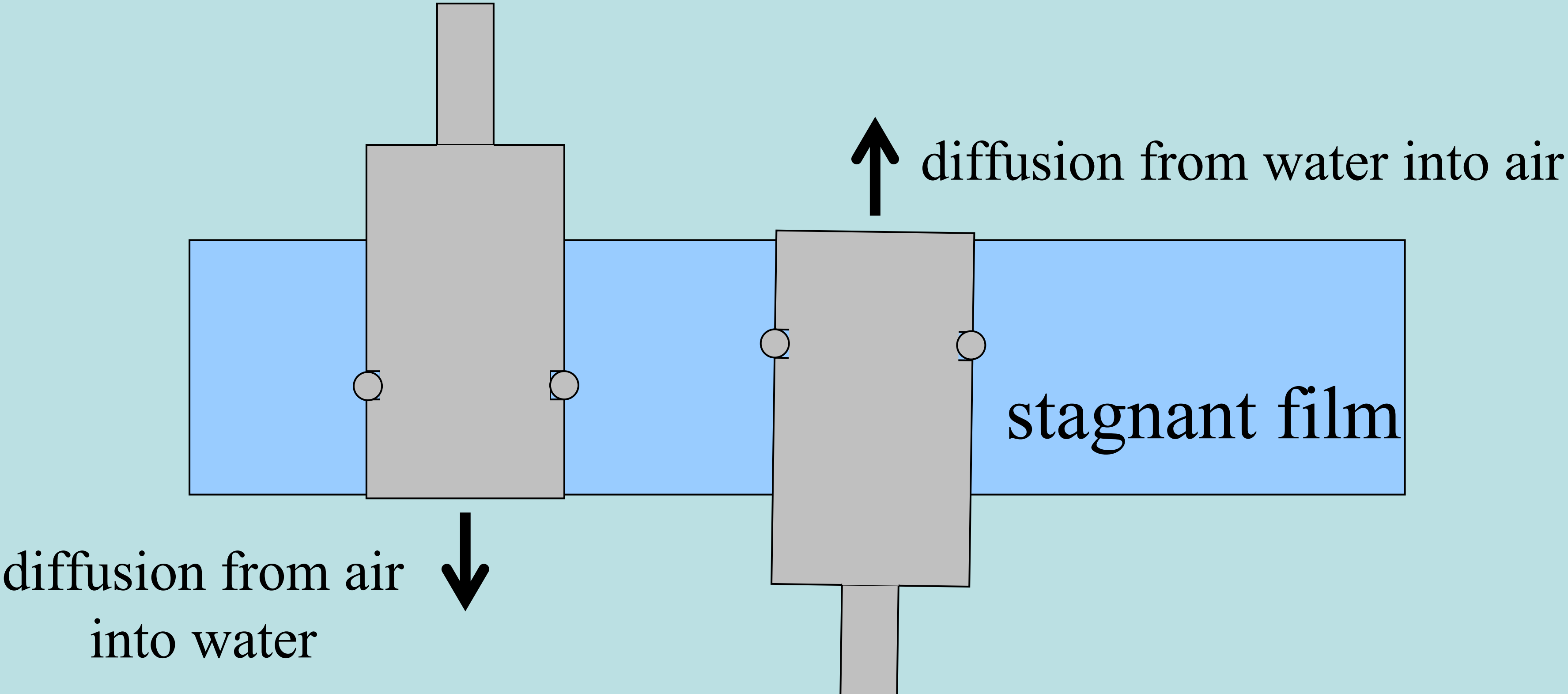
Image removed due to copyright restrictions.
Citation: Figure 3-2. Broecker, W. S., and T. H. Peng. *Tracers in the Sea*. Eldigio Press Lamont Doherty Geological Observatory, 1982, 690 pages.

Note: diffusion is random in direction and gas exchange occurs in both directions. A net flux occurs when there is a concentration gradient where there are more atoms going in one direction than in the other.



# Piston velocity

- D/z has dimensions of velocity
- Gas exchange diffusion through the stagnant film acts as if two pistons, moving in opposite directions, are sweeping the dissolved gases in and out of the stagnant film.
- Piston velocity for $CO_2$ in the ocean is about 2000 m/yr



# $^{222}$Rn deficit method for determining gas exchange rates

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Citation: Figure 3-3. Broecker, W. S., and T. H. Peng. *Tracers in the Sea*. Eldigio Press Lamont Doherty Geological Observatory, 1982, 690 pages.

# Side Track:
# Use of natural radioactivity in studying environmental processes 1

- Radiodecay equations.

- 1. $\frac{dN}{dt} = - \lambda N$

- 2. $N = N_o e^{-\lambda t}$

- 3. The radioactive decay constant is often expressed as a half-life ($t_{1/2}$); i.e., the time it would take for half of the original amount to decay. Setting $N = 1/2\ N_o$ in equation 2, then

- $t_{1/2} = \ln(2) / \lambda = 0.693 / \lambda$

# Use of natural radioactivity in studying environmental processes 2

- The concentrations of radioactive isotopes are often expressed in terms of their activity, i.e., the rate at which the substance undergoes radioactive decay. This has some obvious advantages (you are expressing the concentration in units similar to the measurement device, e.g. a geiger counter, etc., and it immediately tells you how radioactive the substance is) and one less obvious advantage related to the concept of radioactive equilibrium:

- The activity (A) of a radioisotope is defined as:

- $A = dN/dt = \lambda N$

# Use of natural radioactivity in studying environmental processes 3

- 2. Consider a radioactive series consisting of an initial amount of a parent isotope ($P_o$) and radioactive daughter isotope ($D_o$):
- $P \text{ --> } D \text{ -->}$

  $\lambda_P \quad \lambda_D$
- a. For the parent isotope:

  $dP/dt = - \lambda_P P$ ; $P = P_0\, e^{-\lambda p\, t}$
- b. Assuming that at time = 0, $D_1 = 0$, then:

  ...$dD_1/dt = +\lambda_P P - \lambda_D D$ ;
- c. If λP << λD (i.e., the parent is much longer-lived than the daughter), then as t >> $t_{1/2}$ for the daughter isotope (and noting that $P = P_o\, e^{-\lambda p\, t}$),
- $D \cong \lambda_P P / \lambda_D$
- d. That is,

  $\lambda_D D = \lambda_P P$

  $A_D = A_P$
- e. In other words, given a closed system with a long-lived radioactive parent with a succession of shorter-lived radioactive daughter isotopes (and given enough time), the activities of all the isotopes will be equal. Hence we can use activities to estimate whether or not the system has remained closed for the time appropriate to the half-lives of the given isotopes.

# Two references on aspects of radioactivity and radiochemistry:

Friedlander, J.W. Kennedy, E.S. Macias, and J.M. Miller, Nuclear and Radiochemistry, Wiley, N.Y., 684 p.

Faure, G., Principles of Isotope Geology, Wiley, N.Y. , 589 p.

# Global average $CO_2$ exchange rate from natural radiocarbon

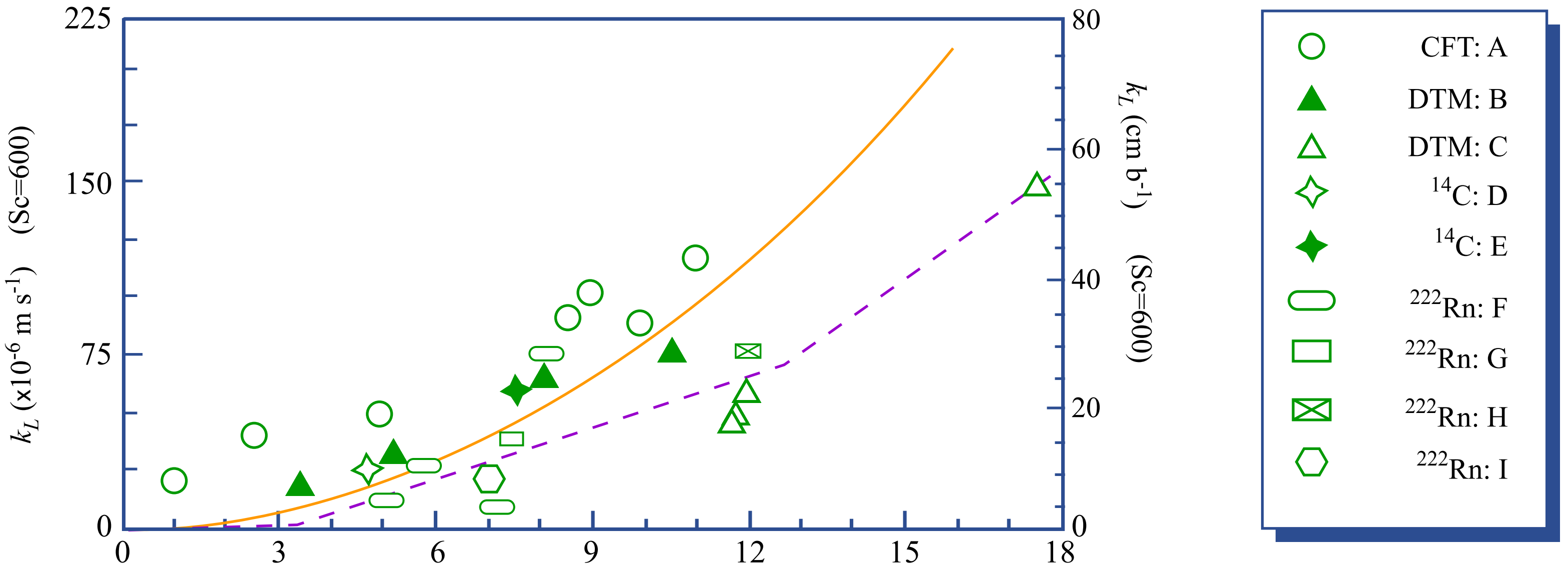
- $^{14}C$ is formed at the top of the atmosphere by the interactions of cosmic rays with atmospheric gases
- This $^{14}C$ is then (well) mixed in the atmosphere and enters the ocean.
- The decay rate of $^{14}C$ in the

  ocean + atmosphere + biosphere ≈ ocean

  is equal to the production rate.
- Hence the flux of $^{14}C$ into the surface ocean must be equal to the difference in radiocarbon concentration between the atmosphere and mixed layer of the ocean.
- So we can calculate $z_{film}$ from natural radiocarbon.

$$z_{film} = \frac{D}{\lambda\ h} \; \frac{[CO_2(aq)]_{surface}}{[\Sigma CO_2]_{ocean}} \; \frac{1 - [C^*/C]_{mixed\text{-}layer} \ / \ [C^*/C]_{atm}}{[C^*/C]_{ocean} \ / \ [C^*/C]_{atm}}$$

# Gas exchange increases with increasing wind speed



Plot of $k_L$ versus $U_{10}$ for representative oceanic measurements of $k_L$ made using the controlled flux technique (CFT), the deliberate tracer method (DTM), bomb $^{14}$C invasion rates, and the $^{222}$Rn method. All measurements have been normalized to Sc=600 assuming that $k_L \propto Sc^{-1/2}$ The wind speed parameterizations of *Wanninkhof* [1992] (solid line) and *Liss* and *Merlivat* [1986] (dashed line) are also shown. Data key shown on the figure, Where A is the CFT data of *Haubecker* ans Jahne [1995], B is the DTM data of *Wanninkhof et al.* [1993], C is the DTM data of *Watson et al.* [1991], D is the bomb $^{14}$C data from *Cember* [1989], E is the bomb $^{14}$C data from *Broecker et al.* [1985], F is the $^{222}$Rn data from *Kromer and Roether* [1983], G is the $^{222}$Rn data from Peng et al. [1979], H is the $^{222}$Rn data from *Peng et al.* [1974], and I is the $^{222}$Rn data from *Broecker and Peng* [1971].

Figure by MIT OpenCourseWare.

# Surfactants can also affect gas exchange

Image removed due to copyright restrictions.
Citation: Figure 4. Asher and Wanninkhof. *JGR* 103 (1998): 15939.

# Recent estimates of gas exchange rate as a function of wind speed

Image removed due to copyright restrictions.
Citation: Figure 8. McGillis, W. R., et al. *Marine Chemistry* 75 (2001): 267-280.

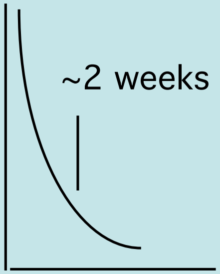
# For a more advanced discussion of the gas exchange process:

- P.S. Liss and L. Merlivat (1986) Air-sea gas exchange rates: introduction and synthesis, in: The Role of Air-Sea Exchange in Geochemical Cycling (ed. P. Buat-Menard et al.), D. Reidel Publishing Co.

- Asher, W., and R. Wanninkhof (1998) Transient tracers and air-sea gas transfer, J. Geophys. Res., 103, 15939-15958,.

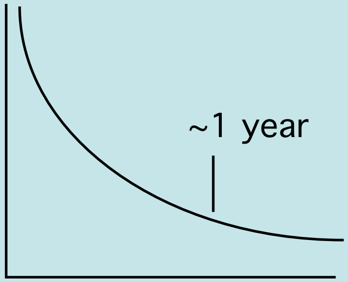
# Equilibration time for atmospheric gases and the ocean mixed layer

Simple Gas Exchange
(e.g. O2, Ar)



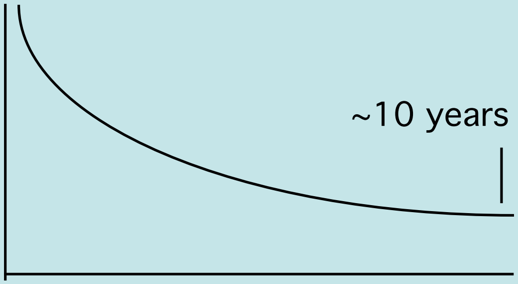
(depth of mixed layer divided by piston velocity - i.e. total gas content divided by gas flux)

pCO2 equilibration



(change in TCO2 required to change pCO2 in seawater is divided by gas flux: e.g. for a 3% increase in pCO2, CO2(aq) rises by 3% and TCO2 rises by 0.3%; but because TCO2 is ~200x CO2(aq), it then takes 200*.3/3=20x longer

carbon isotope equilibration
(C13, C14)



(total carbon dioxide content divided by total gas flux,
~20 moles/m2/yr)

# Outline:

- Seawater $CO_2$ thermodynamics
- Estimating gas exchange rates
  - Thin film model
  - Piston velocity
  - Wind speed dependence
- Ocean $CO_2$ exchange
  - Global $CO_2$ exchange rate
  - Air-sea disequilibrium and spatial variability
- Estimating the penetration of ocean surface waters into the deep ocean
  - Ocean circulation primer
  - Transient tracers
- Estimating ocean uptake of fossil fuel $CO_2$: is there a "missing sink"?
- The $\Delta O_2/\Delta CO_2$ method for estimating ocean and biospheric fossil fuel uptake: quantifying the "missing sink"
- Other methods for observing fossil fuel $CO_2$ uptake
  - $\delta^{13}C$
  - "excess $CO_2$"
  - Historical proxy methods: $\delta^{13}C$ in tree rings and corals
- Extrapolating fossil fuel into the future

# Rate of exchange of $CO_2$ between ocean and atmosphere:

$$2000\ \mathrm{m\ yr^{-1}} * 10^{-5}\ \mathrm{moles\ kg^{-1}} * 1000\ \mathrm{kg\ m^{-3}} = \ 20\ \mathrm{moles\ m^{-2}\ yr^{-1}}$$

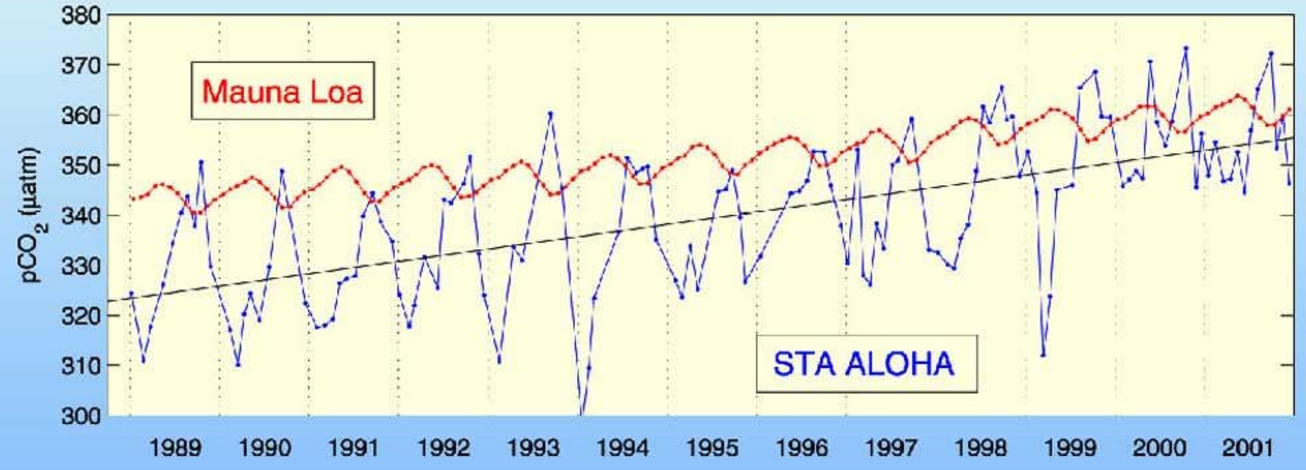
|  |  |  |  |
|---|---|---|---|
| Piston velocity | conc. of gaseous dissolved $CO_2$ | conversion factor | Exchange rate of $CO_2$ across air/sea interface |

# $CO_2$ can show strong short-scale variability

(e.g. the North Atlantic ocean)

Image removed due to copyright restrictions.
Citation: Figure 1. Watson, Andrew J., C. Robinson, J. E. Robinson, P. J. Leb. Williams, and M. J. R. Fasham. "Spatial Variability in the Sink for Atmospheric Carbon Dioxide in the North Atlantic 50." *Nature* 350 (March 7, 1991).

# Change of pCO$_2$ at the ocean surface at the JGOFS station HOT over the 13 years period, 1989 -2002



D.Karl,JGOFS Ocean Science Conference
Washington DC, May 2003

Courtesy of David Karl, University of Hawaii at Manoa. Used with permission.

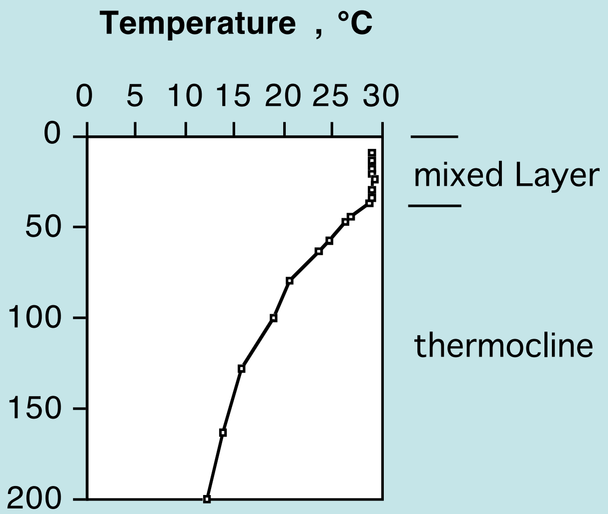
Image removed due to copyright restrictions.
Citation: see image about mean annual flux for 1995 on http://www.ldeo.columbia.edu/res/pi/CO2/.

# Estimating Ocean of Fossil Fuel $CO_2$ Uptake

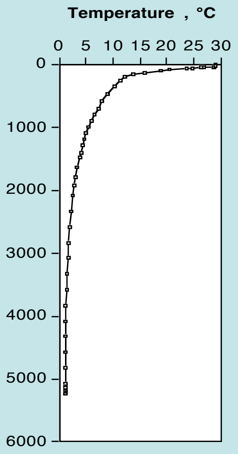
- $CO_2$ in the atmosphere equilibrates on a timescale of less than a year. Hence this is not a rate-limiting step (mean life concept).
- The rate-limiting step is the penetration of surface waters into the interior of the ocean.
- In order to estimate ocean $CO_2$ uptake, we need to find out how fast surface waters move into the deep sea.

# Ocean stratification: the thermocline

depth profile from the Northern Indian Ocean (Geosecs Station 400, 9°21'S   95°1'E)

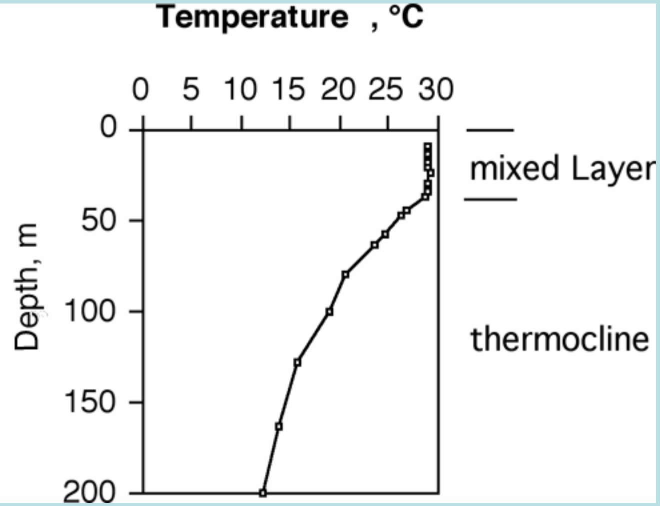


Depth, m

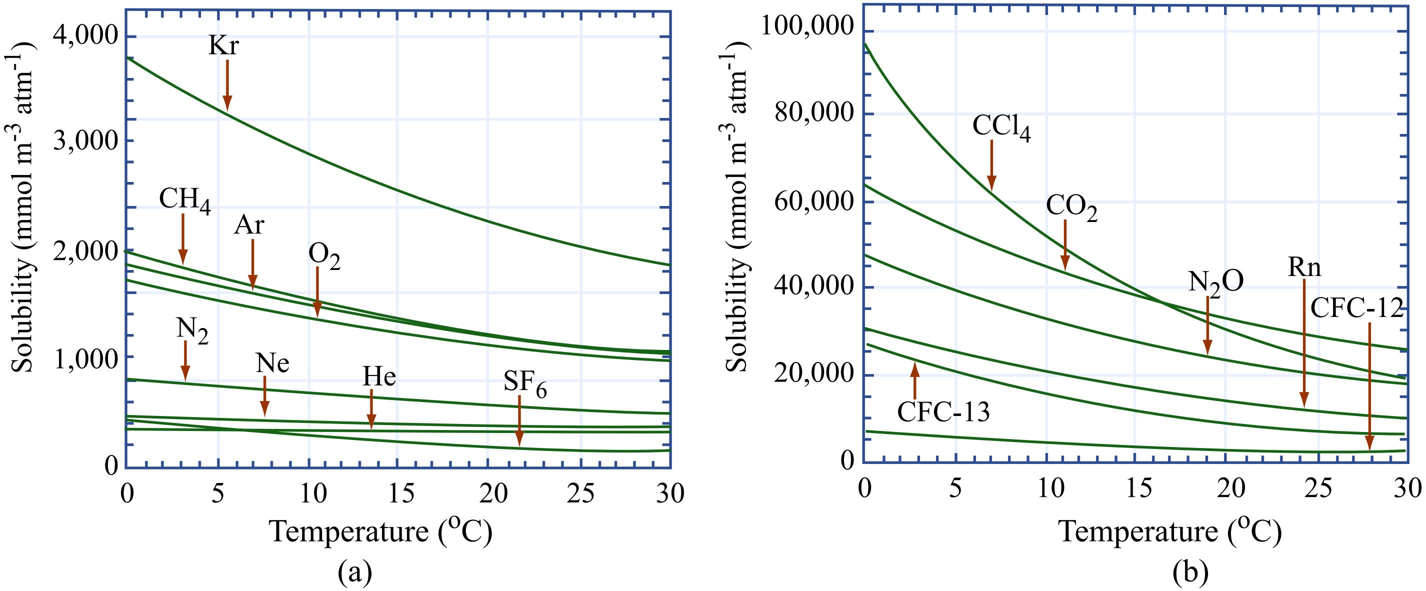


source: GEOSECS

# The carbon “solubility pump”



<u>The solubility pump</u>**:** $CO_2$ is more soluble in cold waters than in warm waters (the thermal pump), and more soluble in fresher waters than saltier waters (the salt pump). If alkalinity were uniform throughout the ocean and if both cold and warm surface waters equilibrated their $p_{CO2}$ with the atmosphere, then cold surface waters would have a higher dissolved carbon dioxide content than warm surface waters. As these cold surface waters circulate into the deep interior of the ocean, deep waters will have more $CO_2$ than warm surface waters.



Plot of the solubility of various gases as a function of temperature. The solubility of all gases decreases with increasing temperature, but there exist large differences in the solubility of the different gases for a particular temperature. These differences can be understood in terms of their molecular weight (ideal gas) or other factors, such as molecular interactions between the gas and the water (nonideal gas). Note the change in vertical scale between panels (a) and (b). Based on the empirical functions listed in table 3.2.2.

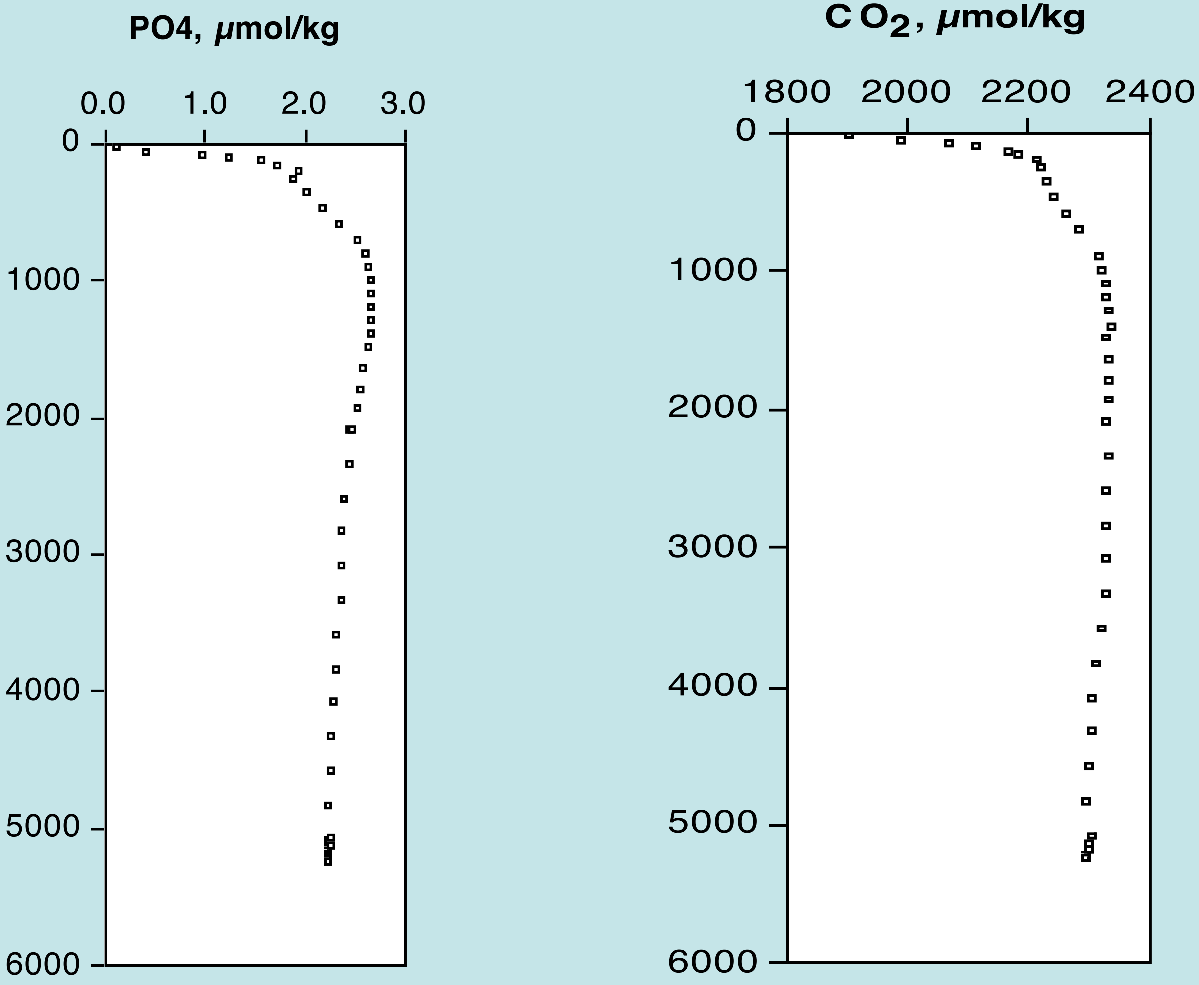
Figure by MIT OpenCourseWare.

Source: Sarmiento and Gruber (2006)

# The carbon "biological pump"

- The biological pump**:** organisms remove carbon and nutrient elements from the surface ocean (which is equilibrated with atmospheric oxygen; note oxygen solubility is a function of temperature); the debris from these organisms sinks and decomposes, releasing carbon and nutrient elements into the deep water and consuming oxygen.
  - **classical Redfield Ratio**:
- $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2 \rightarrow 106CO_2 + 16HNO_3 + H_3PO_4$
- This stoichiometry proposed by Redfield is based on elemental ratios he observed in ocean water samples and plankton. It considers marine organic matter as if it were a mixture of carbohydrates ($CH_2O$), proteins (containing $NH_3$), and phospholipids and nucleic acids ($H_3PO_4$ bearing). In reality, a broad mixture of compounds occur, and the observed stoichiometry $\Delta O_2 : \Delta C$ in deep ocean waters implies a higher value (~165), because of the presence more hydrocarbon-like functional groups:
- $(CH_2O)_{111}(CH_4)_{11}(NH_3)_{16}(H_3PO_4) + 165\ O_2 = 122\ CO_2 + 16\ HNO_3 + 149\ H_2O + H_3PO_4$
- Note the production of nitric and phosphoric acid in this process; this acid changes alkalinity. Once you acknowledge this process, you also need to take into account another effect that reduces the acid effect on alkalinity by about $^1/_3$: the presence of ion-exchanged carboxyl groups:
  - $(CH_2O)_{102}(CH_4)_{14}(HCOO\text{-}Na+)_6(NH_3)_{16}(H_3PO_4) + 165\ O_2$
    - $= 122\ CO_2 + 16\ HNO_3 + 146\ H_2O + H_3PO_4 + 6\ NaOH$
- There is debate on whether the C:P and N:P stoichiometries are fundamental to marine ecosystems, or whether there is some plasticity (e.g., could N:P = 25?). (There is less debate on variable C:N ratios than for C:P).
- We should also note that some organisms precipitate inorganic shells out of calcium carbonate ($CaCO_3$) and silica ($SiO_2 \cdot nH_2O$). For example for every 106 organic carbon atoms converted to organic matter, about 22 $CaCO_3$ molecules are precipitated (ocean-wide average).

# Net result of the solubility and biological carbon pumps:



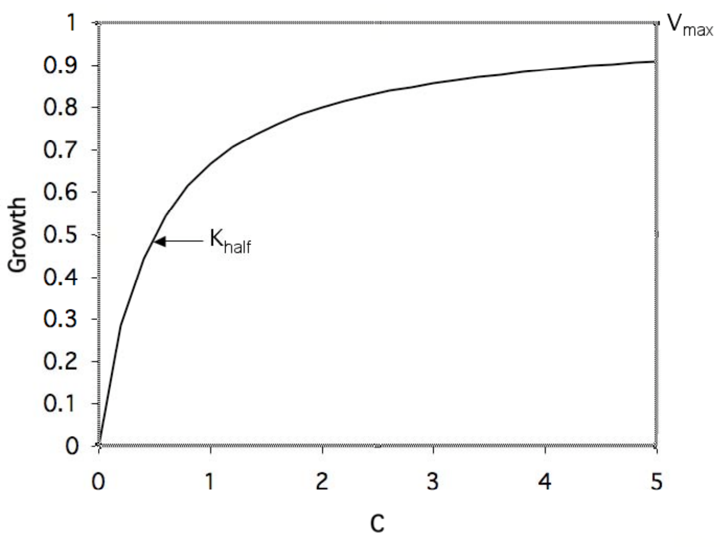
*(tropical ocean)*

# Limiting nutrients

- Concept of the “limiting nutrient”: When light and sufficient nutrients are present, organisms will grow until they deplete the “limiting” nutrient to concentrations that are so low that biological uptake is severely limited. The effect of nutrient concentrations on biological growth is often likened to the “Michaelis-Menten” function (used for representing enzymatic activities)

$$Growth = V_{\max} \frac{C}{C + K_{half-saturation}}$$

  - where C is the concentration of the nutrient and $K_{\text{half-saturation}}$ is the concentration at which the growth rate is half of its maximum value $V_{\max}$



Classically, marine biologists have considered nitrate as the limiting nutrient in most environments (with phosphorus close behind). However, within the past two decades it has been shown that in some environments (so-called “high nutrient low chlorophyll” HNLC), iron is more limiting than nitrogen or phosphorus. Some other trace micronutrients may also be important in some situations (e.g., Zn, Co).