Global Carbon Cycle
AOSC 434/658R & CHEM 434/678A

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2009

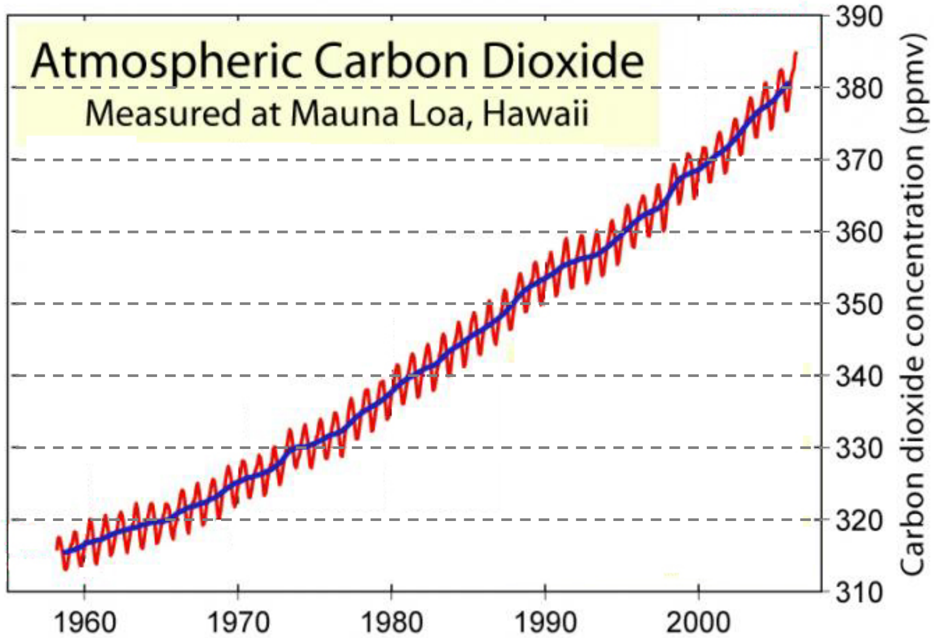
Goals for today:

- **Overview of the Global Carbon Cycle, "scratching below the surface" of the material covered in the readings**
- **Complexities of oceanic and land uptake of CO_2**
- **Connection to prior material (ΔF & ΔT)**
- **Connection to field research**

Lecture 06

17 February 2009

Modern CO_2 Record



Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
http://icestories.exploratorium.edu/dispatches/wp-content/uploads/2008/05/keeling_graph.jpg

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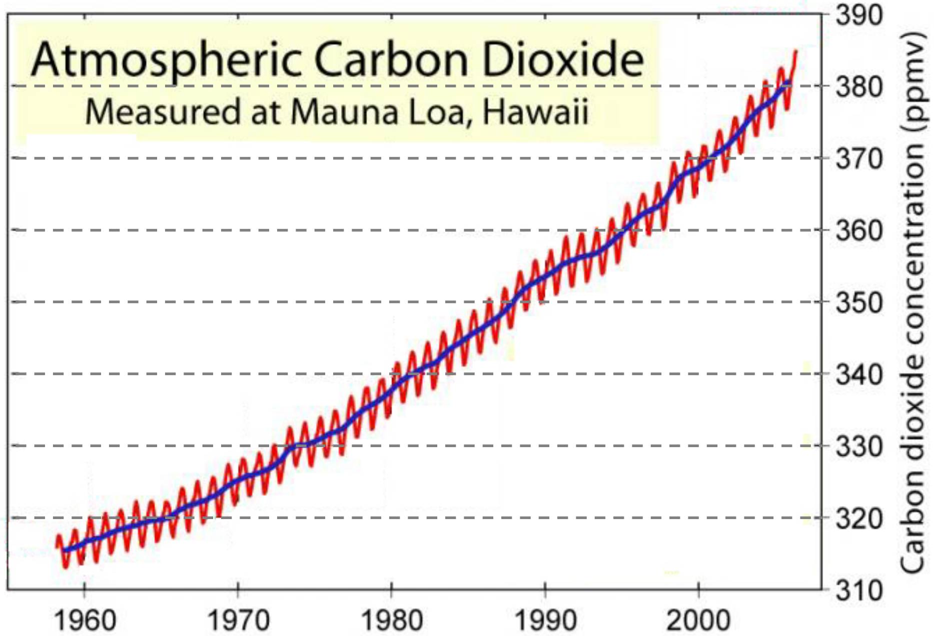
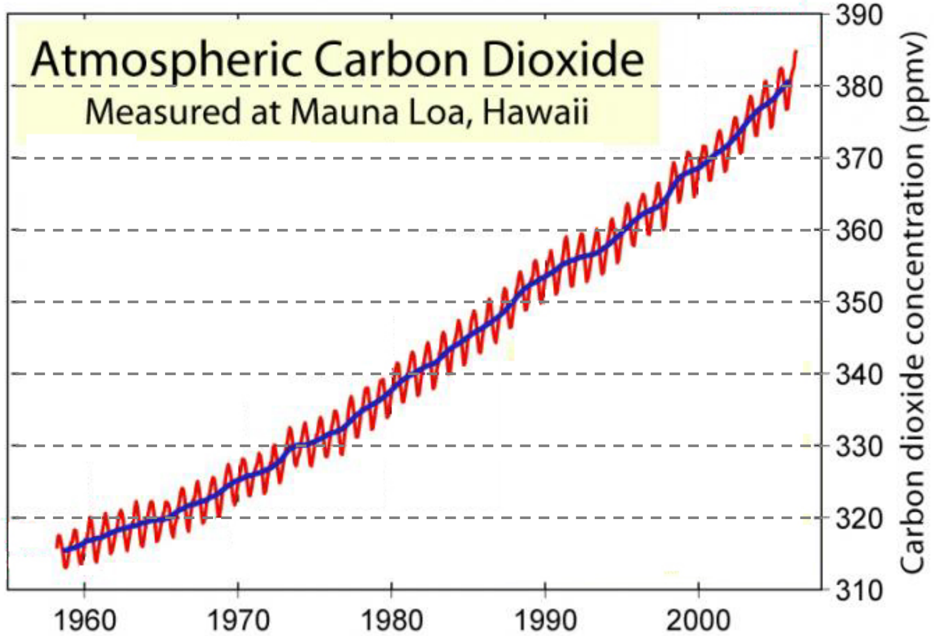


Δ (CO_2) years 1958 to 2005 = 379.7 – 315.1 ppm
= 64.6 ppm

Modern CO_2 Record



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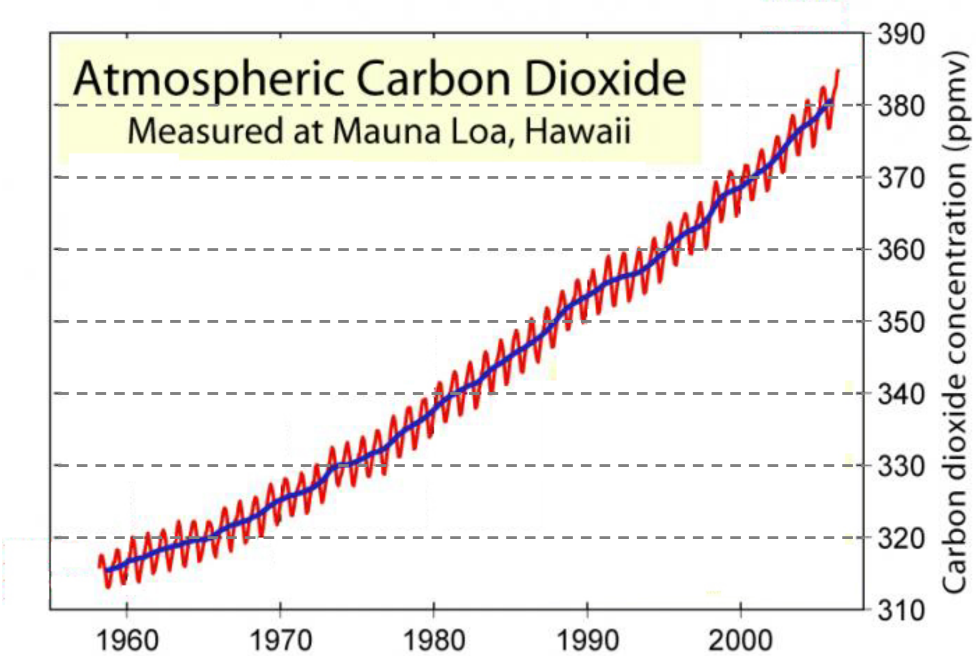
ΔF = ?

Modern CO_2 Record



Δ (CO_2) years 1958 to 2005 = 64.6 ppm

$\Delta F = 5.36\ Wm^{-2}\ \ln(379.7/315.1) = 1.00\ Wm^{-2}$

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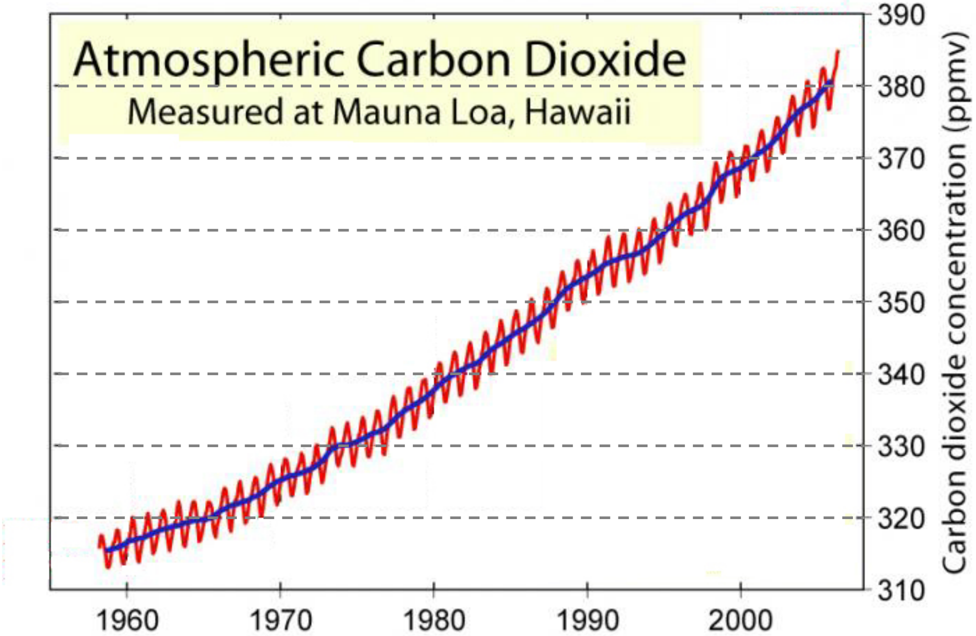

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ΔT = ?

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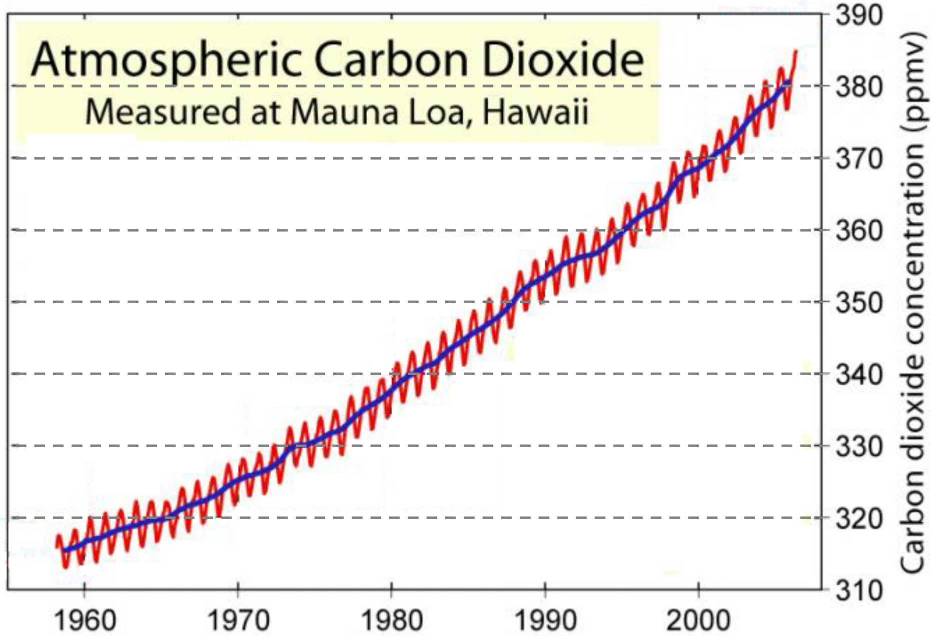

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$\Delta T = \lambda\ \Delta F = 0.57\ K\ /\ W\ m^{-2}\ \Delta F = 0.57\ K$

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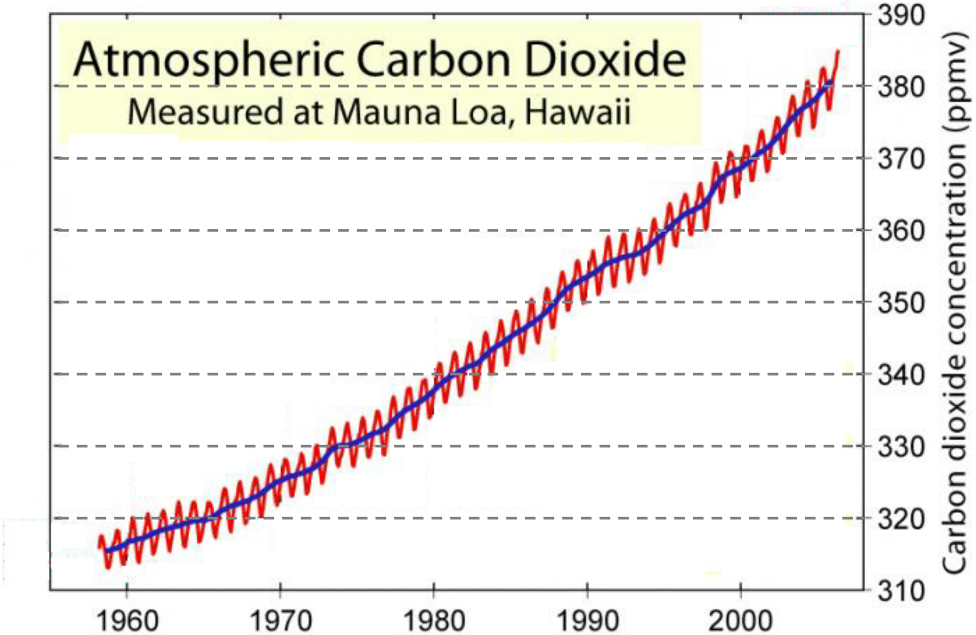

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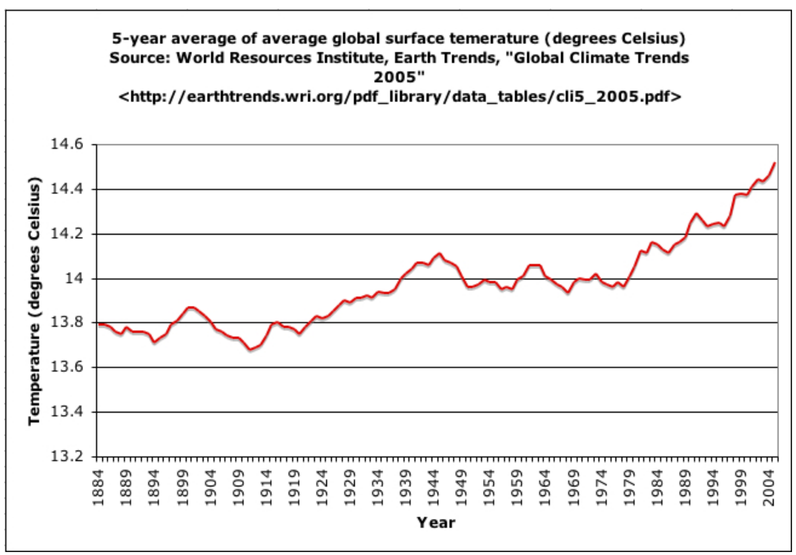
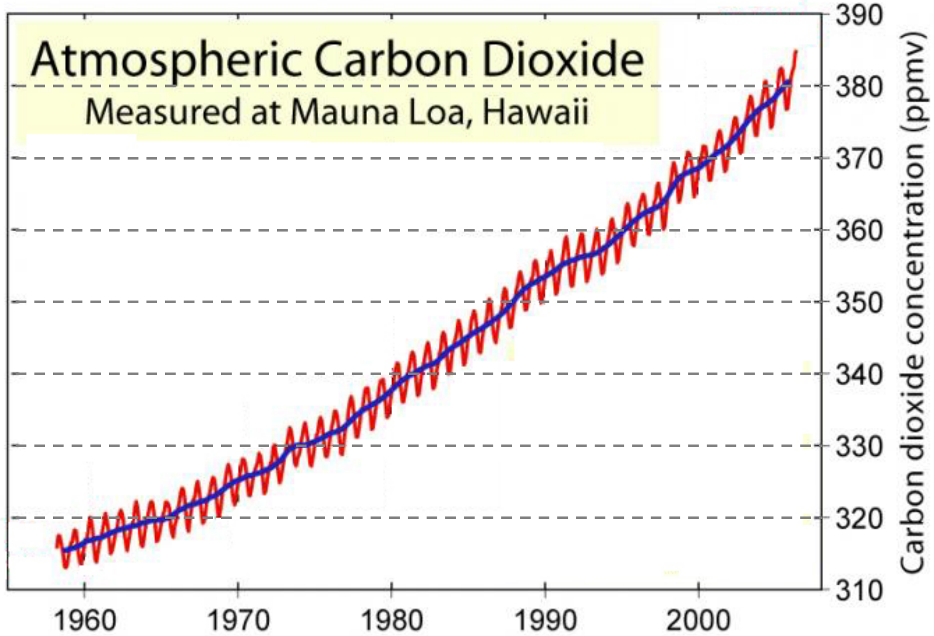


http://www.chelseagreen.com/content/wp-content/avg_global_temperature.jpg

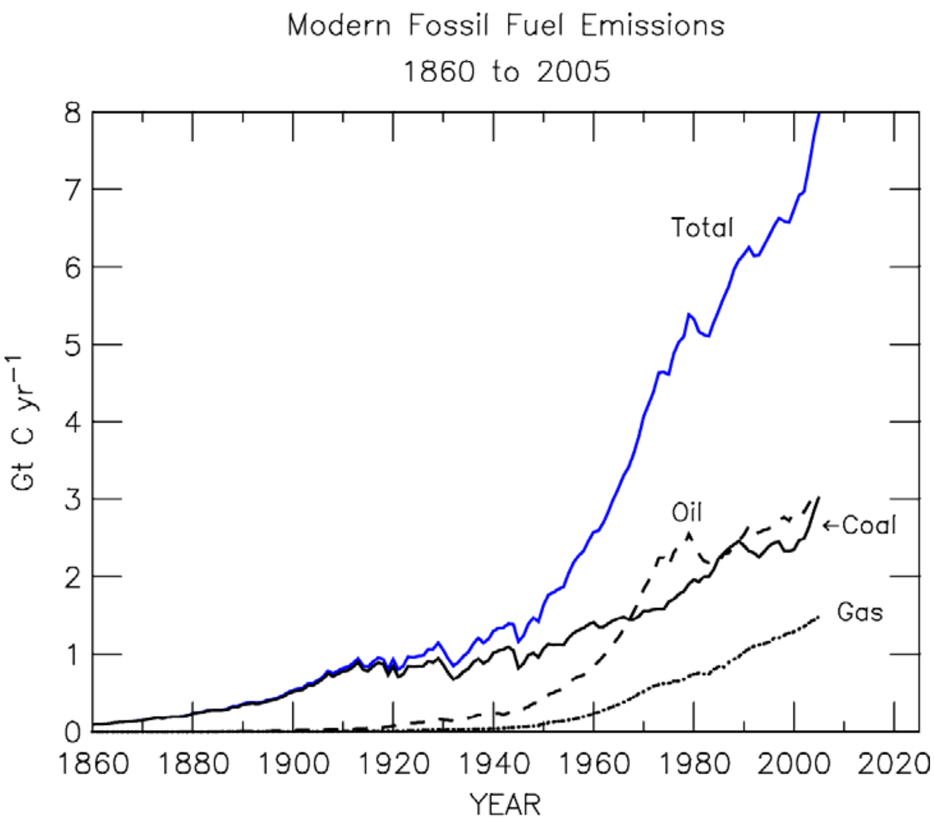
Modern CO_2 Record



1 ppm $CO_2 \approx 10^{-6} \times 5.27 \times 10^{21}$ gm $\times$ 12/29 $\times 10^{-6}$ ton/gm
= 2.2×10^{9} tons C
= 2.2 Gt (giga tons) C

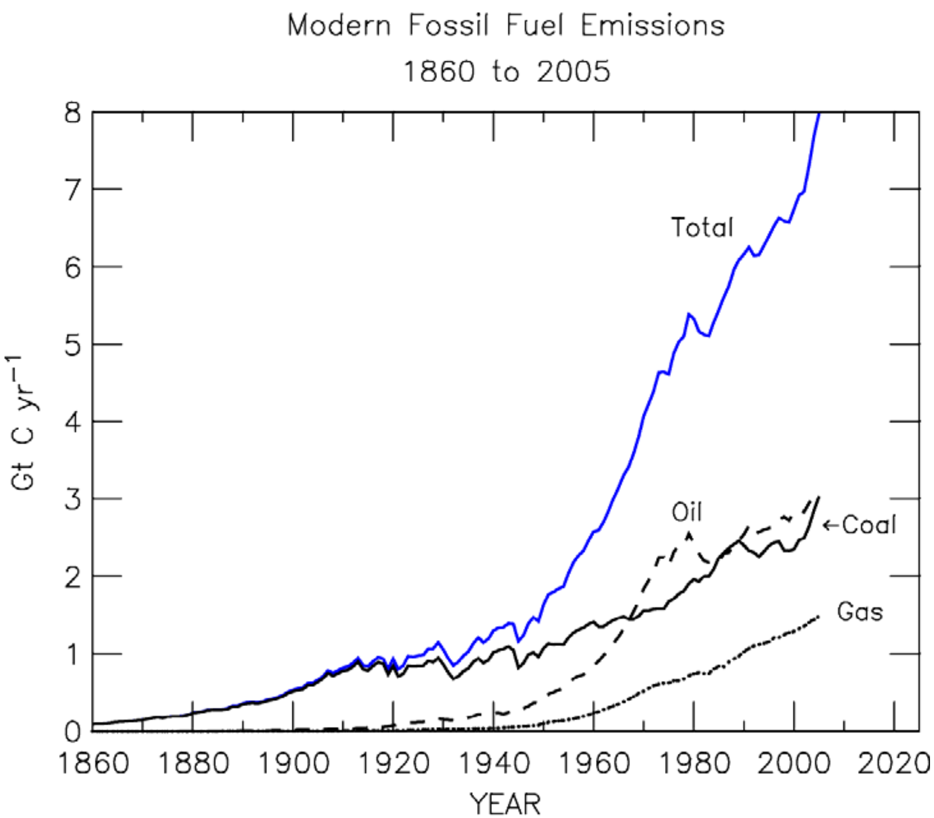
Δ (CO_2) years 1958 to 2005 = 64.6 ppm = 142 Gt C

Global Carbon Cycle



Data from http://cdiac.ornl.gov/ftp/ndp030/global.1751_2005.ems

Global Carbon Cycle



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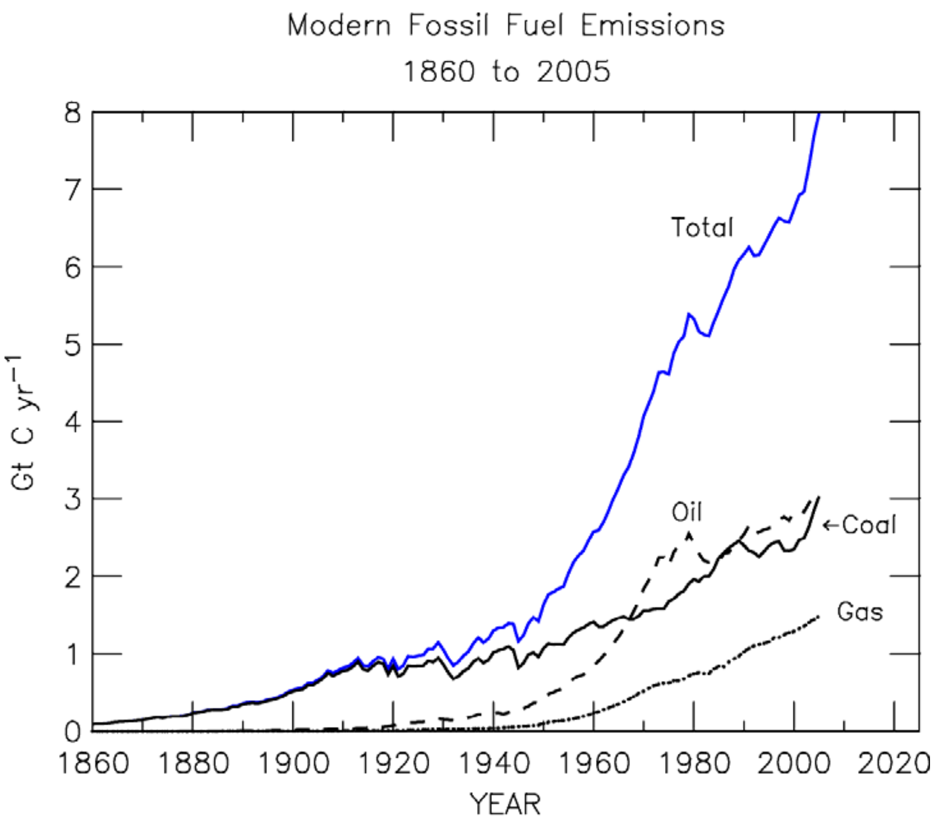
Fossil fuel emissions, 1958 to 2005 = 245 Gt C

Δ (CO_2), 1958 to 2005 = 142 Gt C

Global Carbon Cycle



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Fossil fuel emissions, 1958 to 2005 = 245 Gt C

Δ (CO_2), 1958 to 2004 = 142 Gt C

~60 % of carbon emitted remains in the atmosphere

Rest goes to either:

- oceans
- terrestrial biosphere (trees and plants)

Human Release of Carbon

Current human activities release about 8 Gt (giga tons), or 8,000,000,000 (8×10^9) tons of carbon per year.

How much is 8 Gt of carbon ?!?

Human Release of Carbon

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How much is 8 Gt of carbon ?!?

Mazda Miata weighs about 1 ton (2200 lbs)

8 Gigatons C ≈ 8 billion Miatas

Miata is about 13 feet long

Earth's circumference is ~25,000 miles

⇒ 10 million Miatas placed end-to-end

8 Gigatons C is equivalent to a series of Miatas, placed end-to-end, encircling the Earth 800 times !

World Carbon Emissions

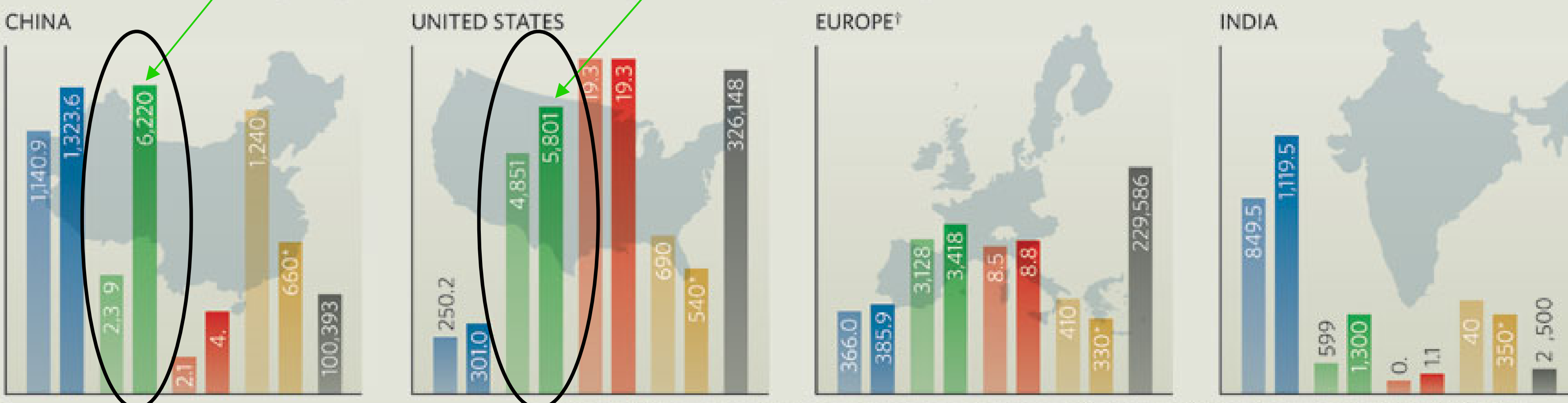
20 June 2007

China: 1.70 Gt C per year

US: 1.58 Gt C per year

Last week, the Netherlands Environmental Assessment Agency produced a preliminary report showing that China had overtaken the United States as the world's largest emitter of carbon dioxide from the burning of fossil fuels and the manufacture of cement (44% of the world's new cement is currently being laid in China). Here's how the world's big emitters stacked up.

In per capita terms, the United States is still easily the most carbon-profligate economy, and it has made by far the largest historical contribution to the stock of atmospheric CO_2. In terms of the emissions it takes to provide a given amount of gross domestic product (GDP), the carbon intensity, China is in the worst position. The carbon intensity has dropped in all four economies since 1990, most impressively in China. But given economic growth, overall global CO_2 emissions rose by more than 35% between 1990 and 2006.

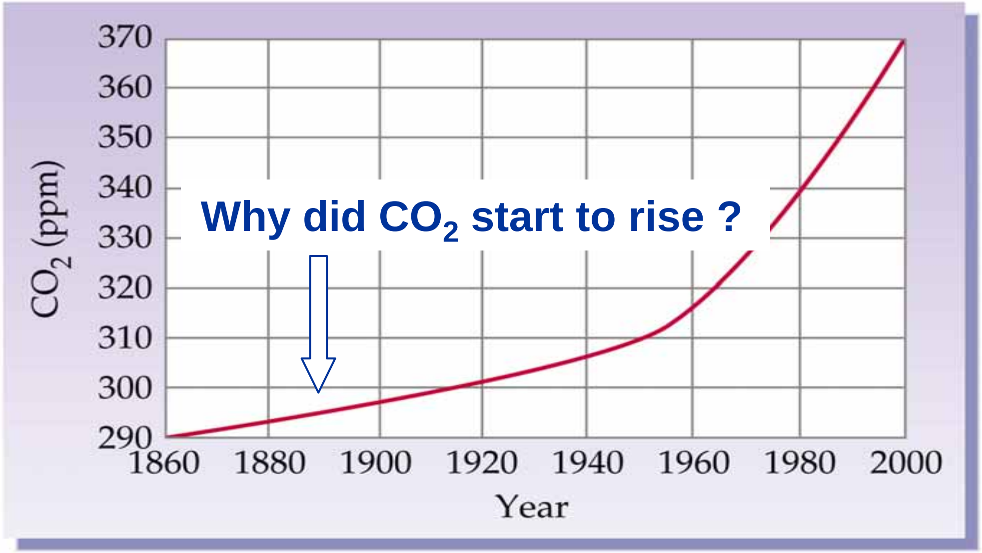


1990 2006

- Population (million)
- Total CO_2 emissions (million tonnes)
- CO_2 emissions per capita (tonnes)
- CO_2 intensity (tonnes per thousand US$ GDP)
- Cumulative CO_2 1900–2006 (million tonnes)

Notes: 2006 figures from Netherlands Environmental Assessment Agency (NEAA) based on recently published BP (British Petroleum) energy data and cement production data by the US Geological Survey. 1990 figures from the International Energy Agency (IEA) and cumulative 1900–2006 emissions (from the NEAA, IEA and World Resources Institute) both exclude cement production. CO_2 intensity figures (from the IEA) are calculated on a purchasing power parity basis using 2000 prices.
*Figures from 2004; †Europe is the 15 members of the European Union as of 1995.

Atmospheric CO_2, 1860 to 2000



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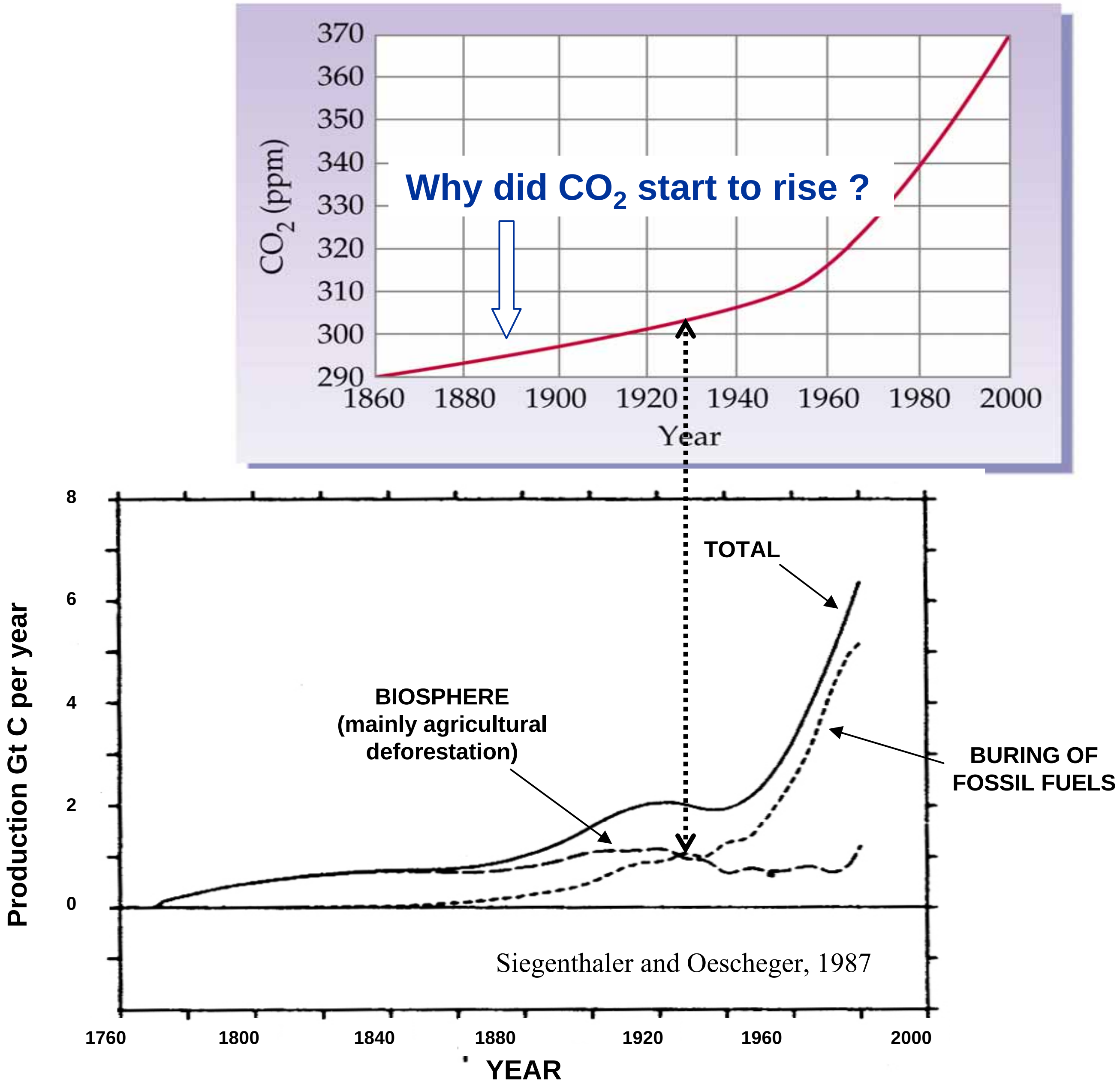

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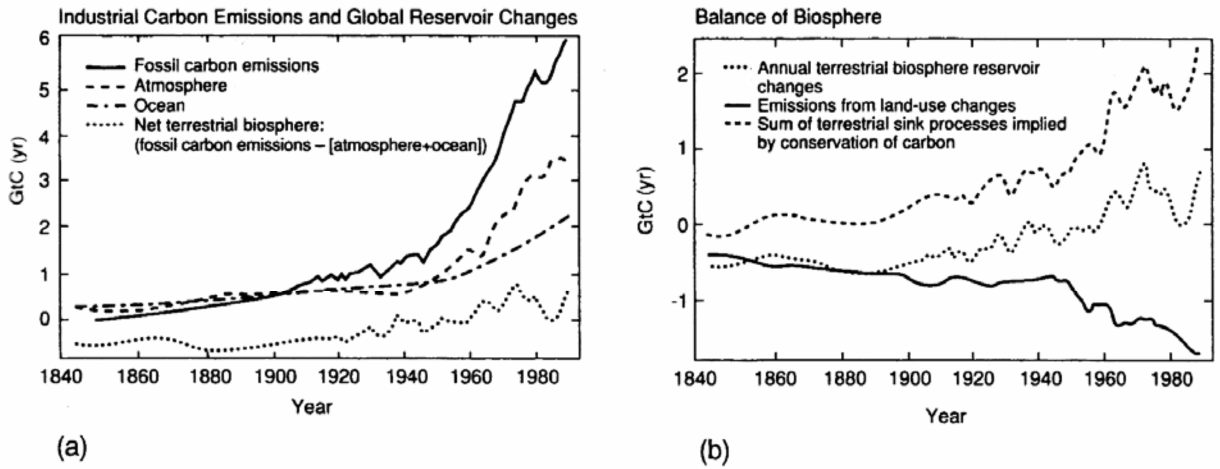


Figure 3.3 (a) Fossil carbon emissions (based on statistics of fossil fuel and cement production) and estimates of global reservoir changes: atmosphere (deduced from direct observations and ice core measurements), ocean (calculated with the Geophysical Fluid Dynamics Laboratory (GFDL), University of Princeton, ocean carbon model) and net terrestrial biosphere (calculated as remaining imbalance) from 1840 to 1990. The calculation implies that the terrestrial biosphere was a net source to the atmosphere prior to 1940 (negative values) and has been a net sink since about 1960. (b) Estimates of contributions to the carbon balance of the terrestrial biosphere. The curve showing the terrestrial reservoir changes is taken from (a). Emissions from land-use changes (including tropical deforestation) are plotted negatively because they represent a loss of biospheric carbon. These estimates are subject to large uncertainties (see uncertainty estimates in Table 3.1).

Global Carbon Cycle

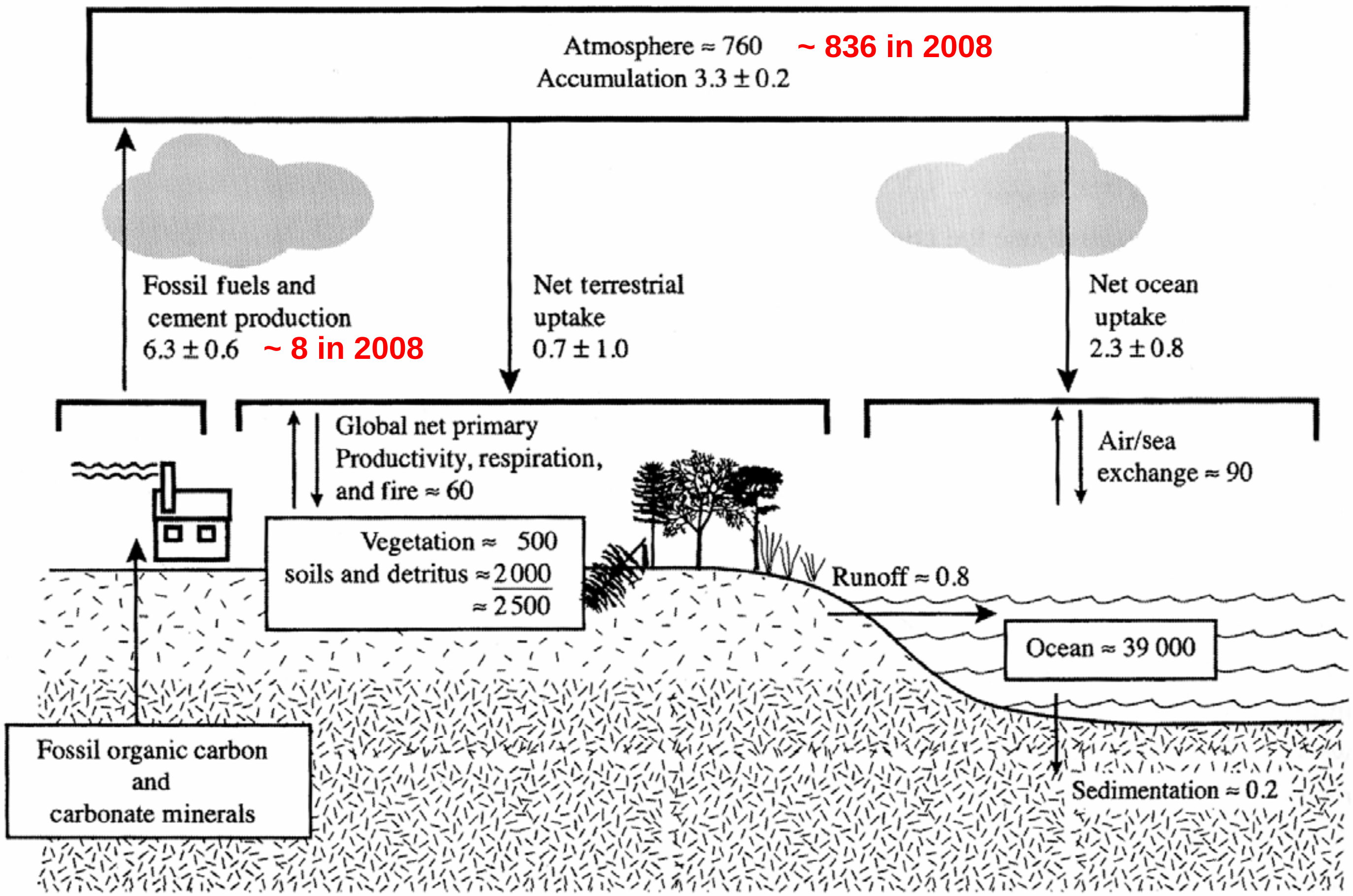


Figure 3.1 The global carbon cycle, showing the carbon stocks in reservoirs (in Gt) and carbon flows (in Gt year^{-1}) relevant to the anthropogenic perturbation as annual averages over the decade from 1989 to 1998. Net ocean uptake of the anthropogenic perturbation equals the net air/sea input plus run-off minus sediment. The units are thousand millions of tonnes or gigatonnes (Gt).

Global Carbon Cycle

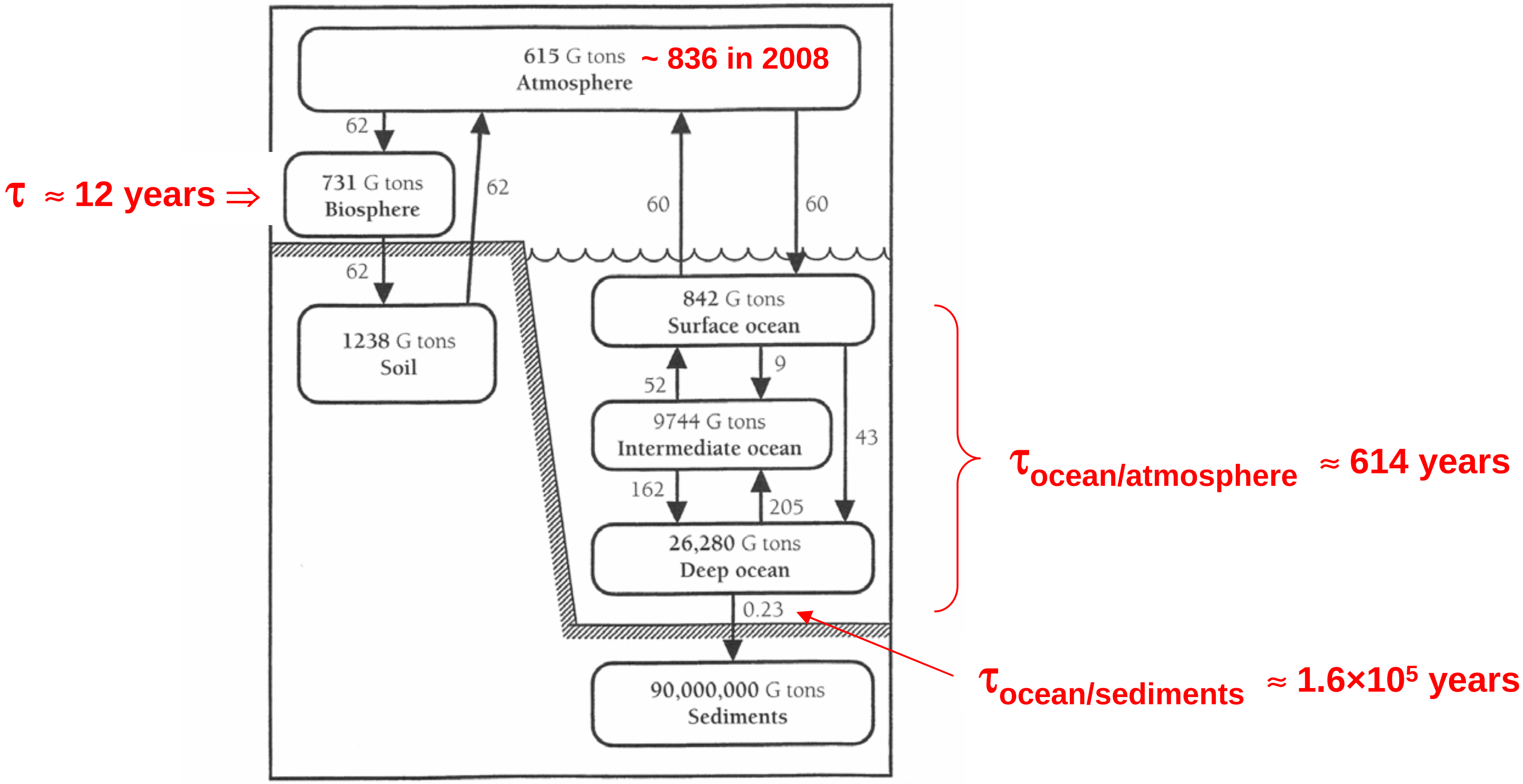


Figure 11.8 Composite model for the global carbon cycle, combining data in Figures 11.5 and 11.6. Reservoir contents are in units of 10^9 tons C; transfer rates are in 10^9 tons C yr^{-1}. Carbon is deposited in sediment both as $CaCO_3$ and as organic matter. There is a small release of CO_2 in steady state from the ocean; this source is employed in weathering of crustal rocks.

McElroy, The Atmospheric Environment, 2002

CO_2 Is Long Lived

Table TS.2. *Lifetimes, radiative efficiencies and direct (except for CH_4) global warming potentials (GWP) relative to CO_2. {Table 2.14}*

Industrial Designation or Common Name (years)	Chemical Formula	Lifetime (years)	Radiative Efficiency ($W\ m^{-2}\ ppb^{-1}$)	Global Warming Potential for Given Time Horizon: SAR‡ (100-yr)	20-yr	100-yr	500-yr
Carbon dioxide	CO_2	See below[a]	[b]1.4×10^{-5}	1	1	1	1
Methane[c]	CH_4	12[c]	3.7×10^{-4}	21	72	25	7.6
Nitrous oxide	N_2O	114	3.03×10^{-3}	310	289	298	153

Notes:

‡ SAR refers to the IPCC Second Assessment Report (1995) used for reporting under the UNFCCC.

[a] The CO_2 response function used in this report is based on the revised version of the Bern Carbon cycle model used in Chapter 10 of this report (Bern2.5CC; Joos et al. 2001) using a background CO_2 concentration value of 378 ppm. The decay of a pulse of CO_2 with time t is given by

$$a_0 + \sum_{i=1}^{3} a_i \cdot e^{-t/\tau_i}$$ where $a_0 = 0.217$, $a_1 = 0.259$, $a_2 = 0.338$, $a_3 = 0.186$, $\tau_1 = 172.9$ years, $\tau_2 = 18.51$ years, and $\tau_3 = 1.186$ years, for $t < 1{,}000$ years.

[b] The radiative efficiency of CO_2 is calculated using the IPCC (1990) simplified expression as revised in the TAR, with an updated background concentration value of 378 ppm and a perturbation of +1 ppm (see Section 2.10.2).

[c] The perturbation lifetime for CH_4 is 12 years as in the TAR (see also Section 7.4). The GWP for CH_4 includes indirect effects from enhancements of ozone and stratospheric water vapour (see Section 2.10) .

from IPCC 2007 "Physical Science Basis"

CO_2 has multiple time constants

Longest decay is close to 200 years:
time for surface waters to equilibrate with intermediate ocean

CO_2 Is Long Lived

To avoid 2×CO_2 (560 ppm), much less 3×CO_2 (840 ppm), there must be a drop in CO_2 emissions due to the burning of fossil fuel very soon

Curve that levels off at ~550 ppm has emissions peaking in 2027 (20 years from now!)

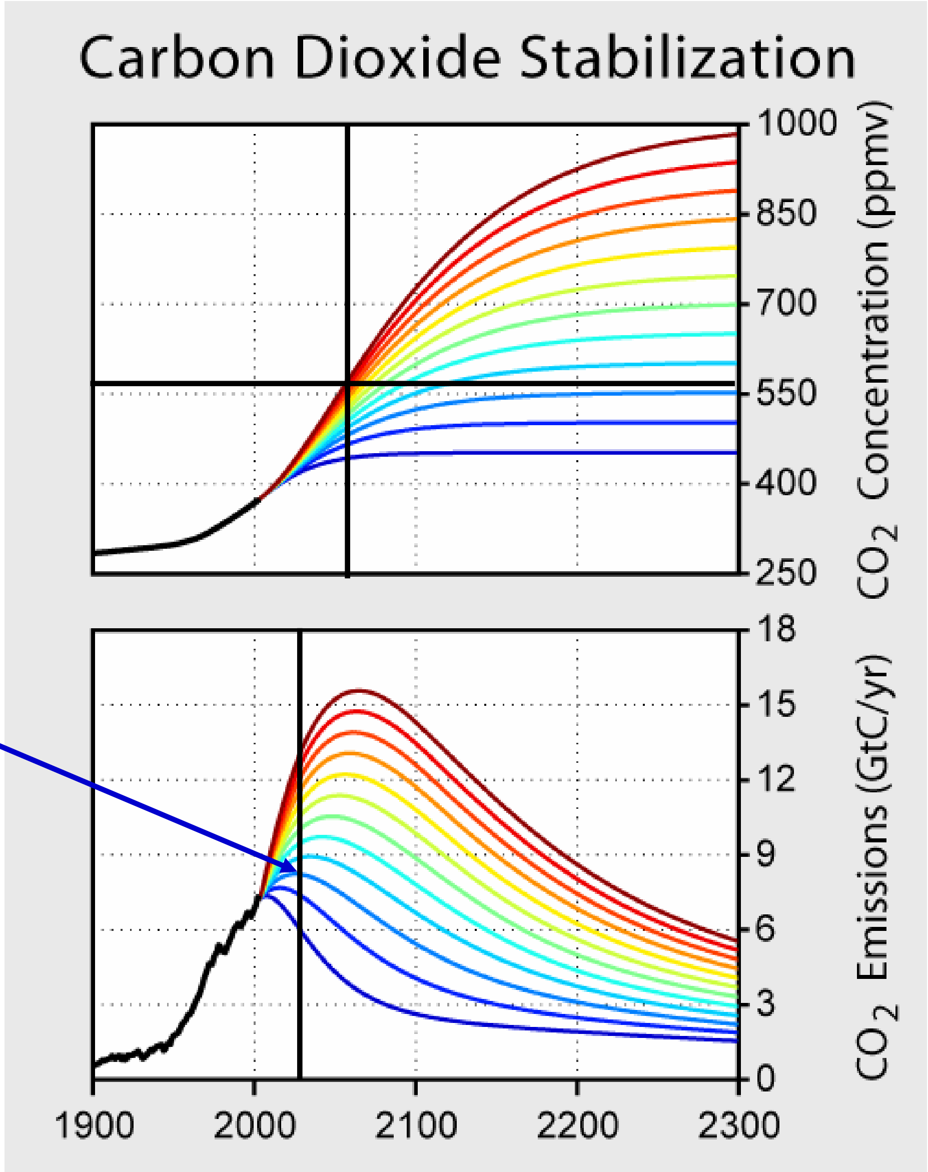


Image: "Global Warming Art": http://www.globalwarmingart.com/wiki/Image:Carbon_Stabilization_Scenarios_png

Global Carbon Cycle

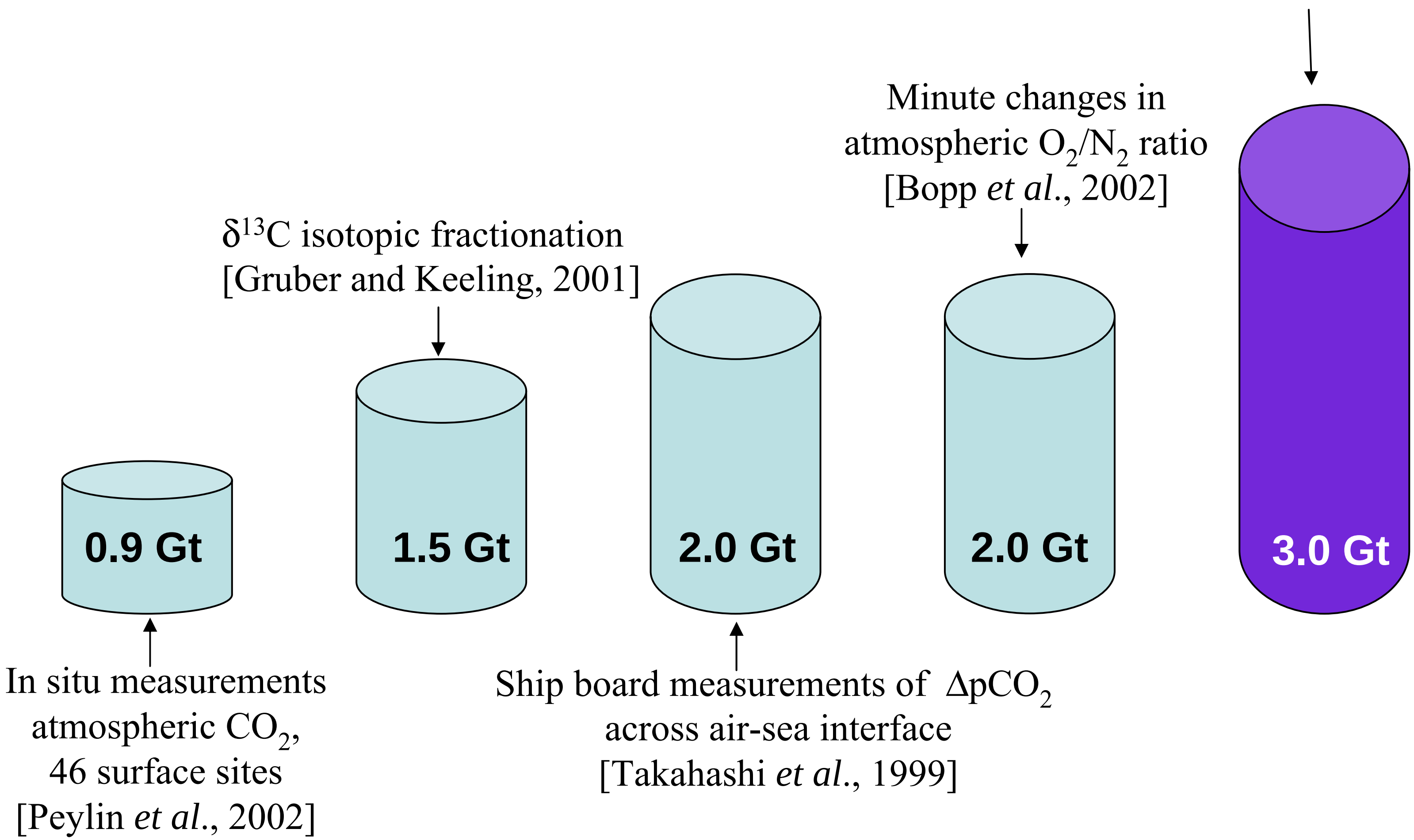
Where is the CO_2 being sequestered?

During the 1990s, humans released ~7 Gt C/yr.

If 60% stays in the atmosphere, then 0.4×7 Gt C/yr $\approx$ **3 Gt C/yr** must be going to land and oceans

Ocean uptake estimated to be:

CARBON SINK



Global Carbon Cycle

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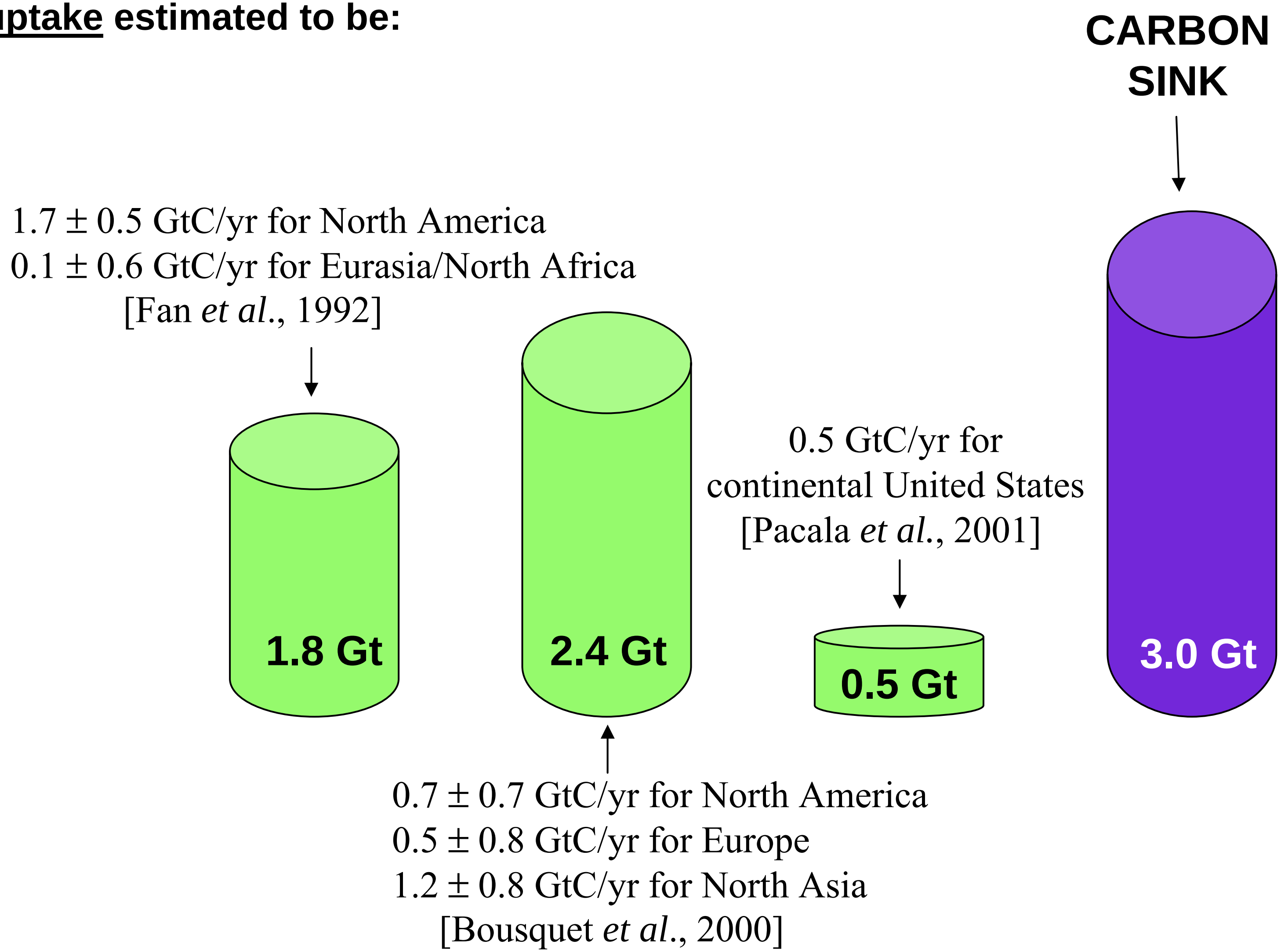
<u>Land uptake</u> estimated to be:



Inferring CO_2 Uptake Based on $\Delta(O_2)$

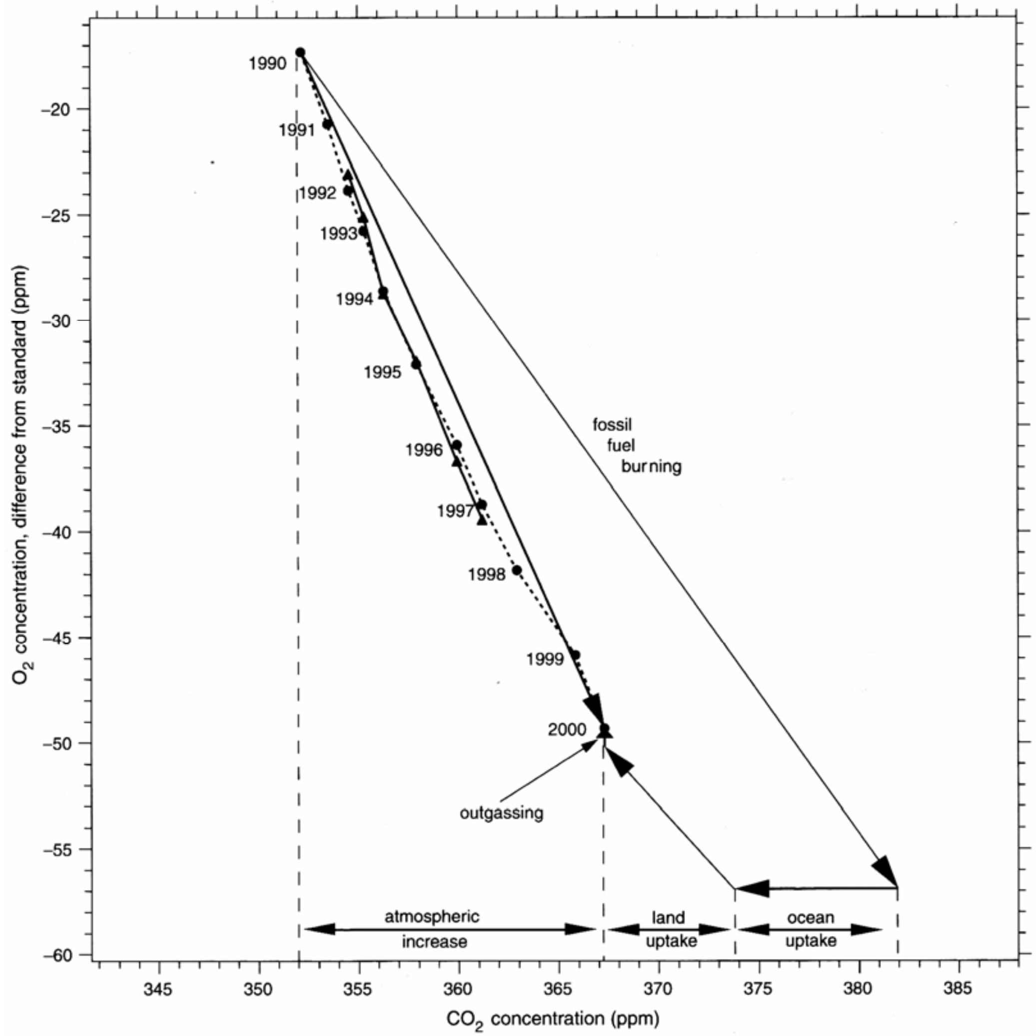


Figure 3.4 Partitioning of fossil fuel carbon dioxide uptake using oxygen measurements. Shown is the relationship between changes in carbon dioxide and oxygen concentrations. Observations are shown by solid circles and triangles. The arrow labelled 'fossil fuel burning' denotes the effect of the combustion of fossil fuels based on the $O_2 : CO_2$ stoichiometric relation of the different fuel types. Uptake by land and ocean is constrained by the stoichiometric ratio associated with these processes, defining the slopes of the respective arrows.

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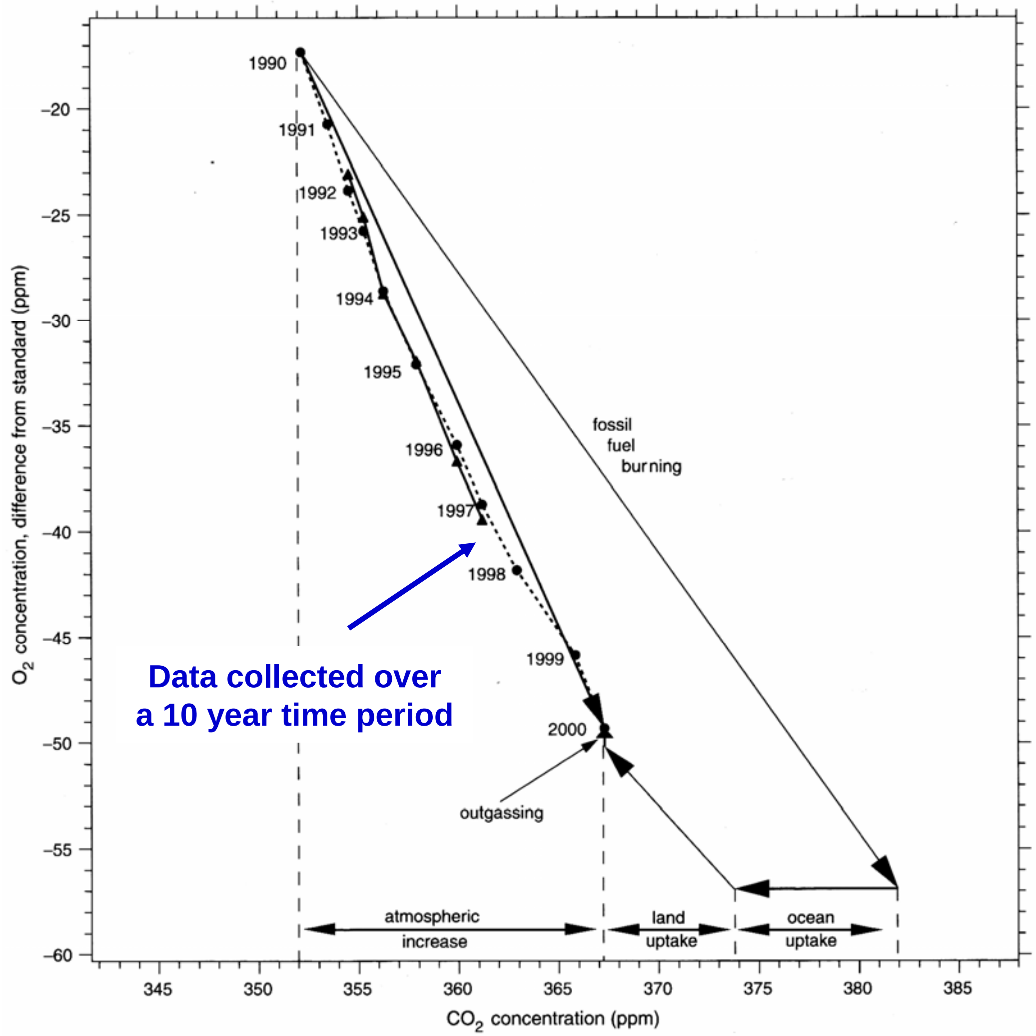

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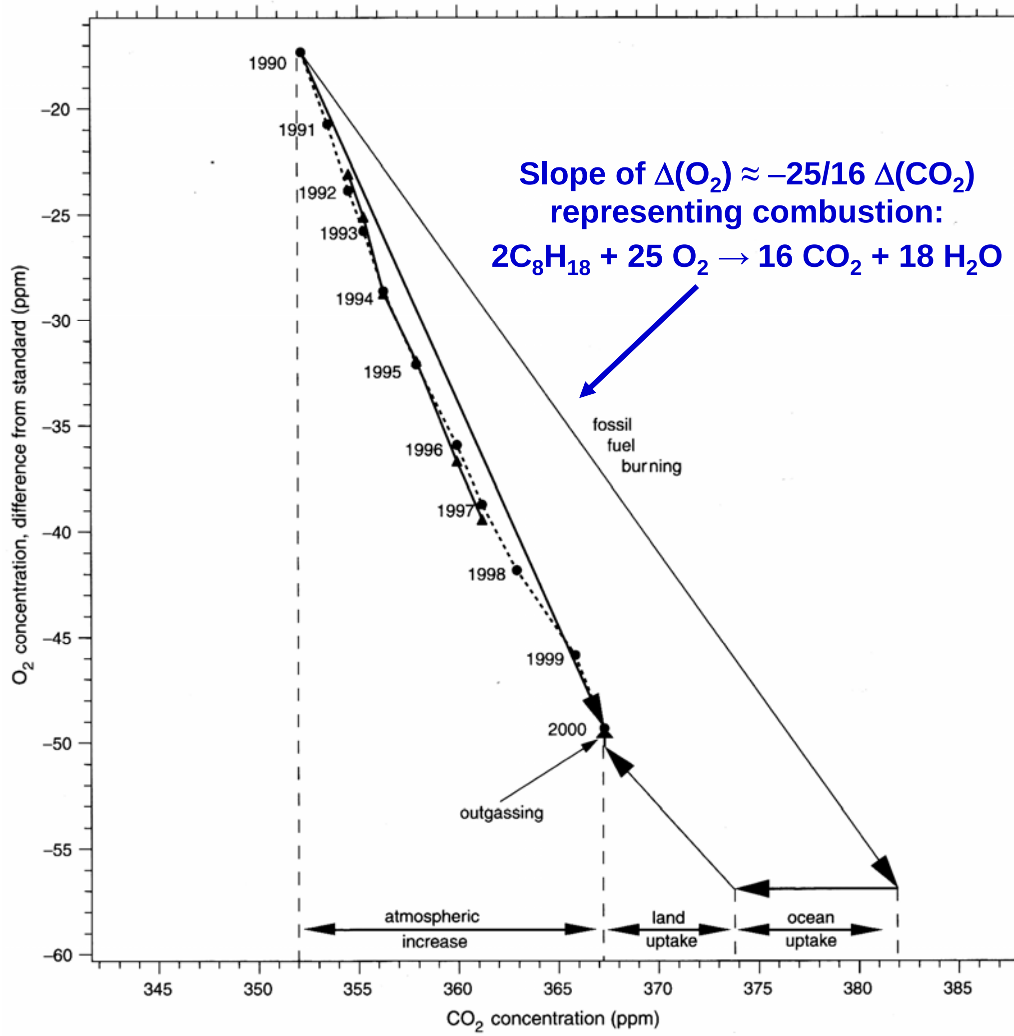

Slope of $\Delta(O_2) \approx -25/16\ \Delta(CO_2)$ representing combustion:
$2C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$

O_2 falls a tiny bit as CO_2 rises

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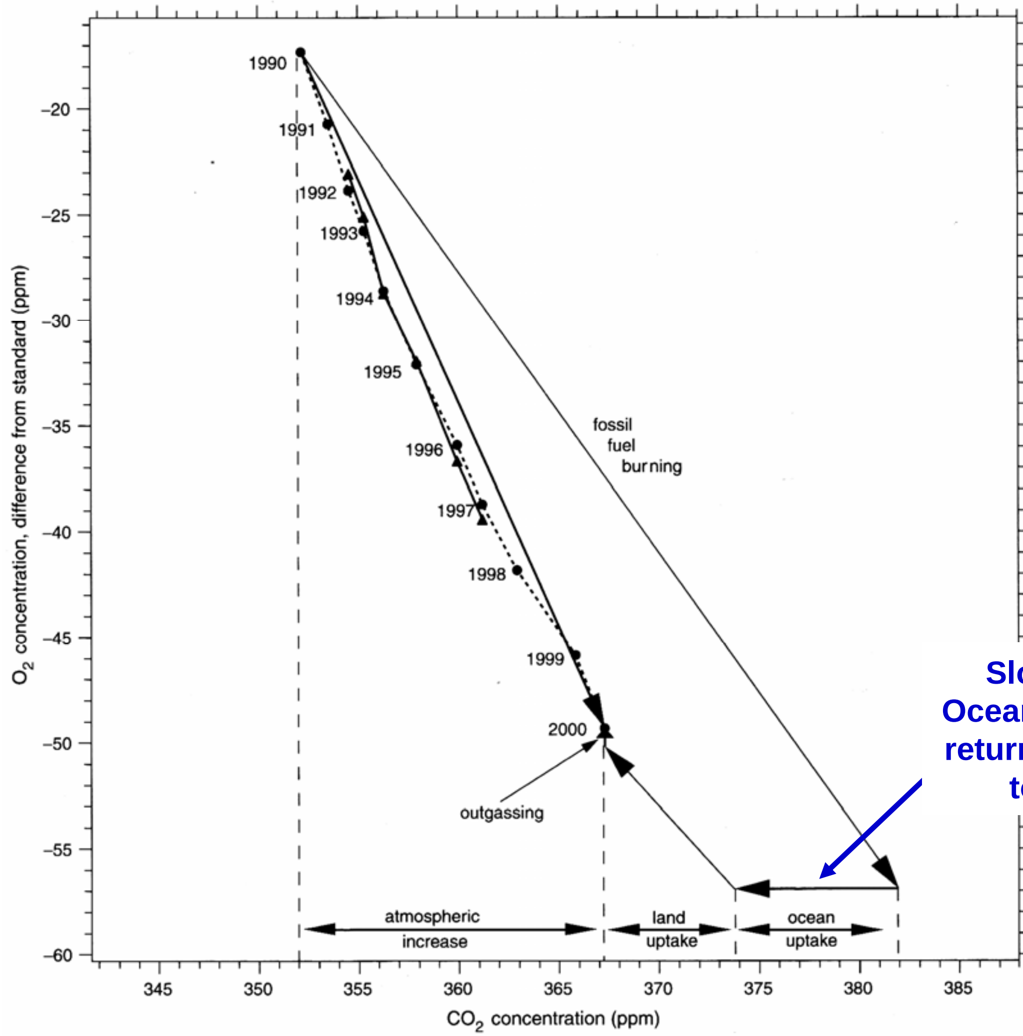

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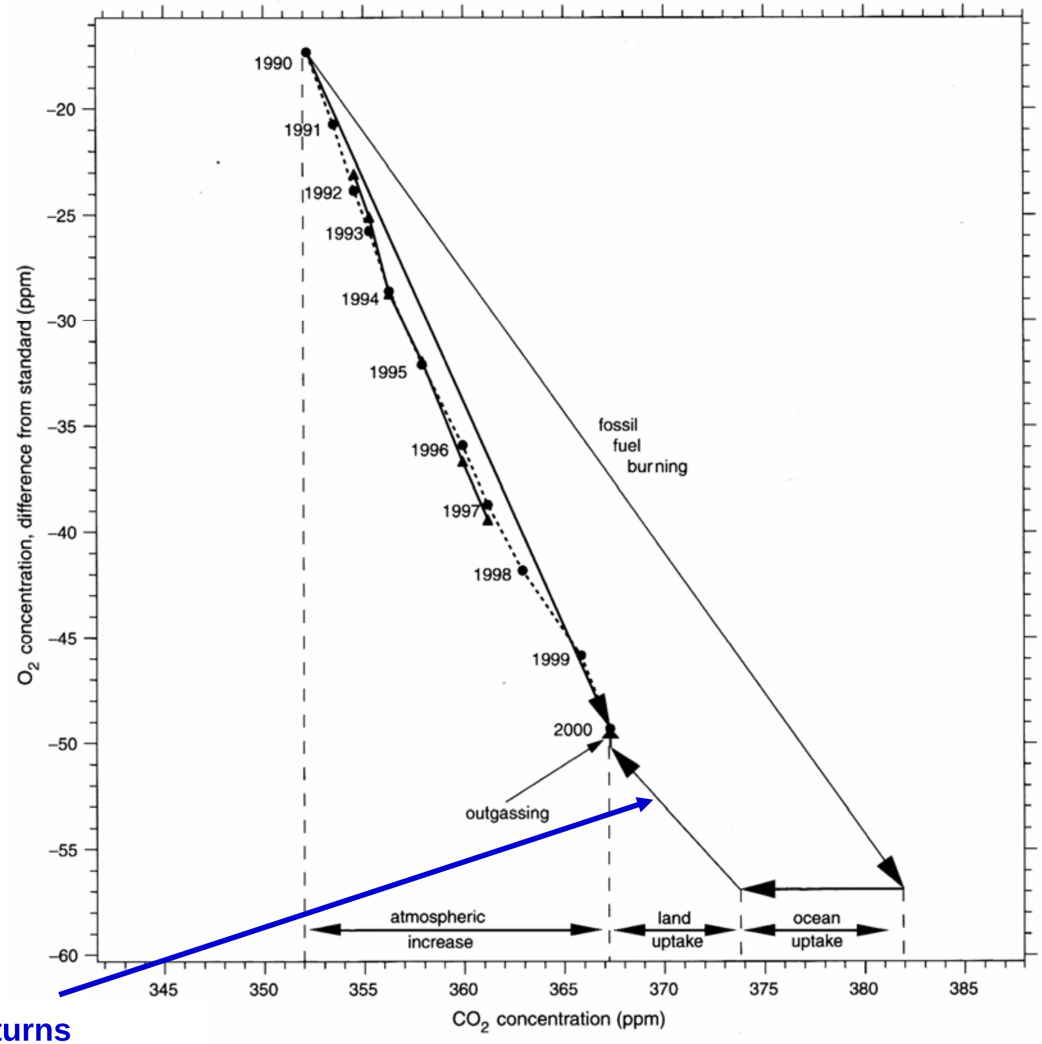
Slope of $\Delta(O_2) = 0$
Ocean Uptake does not return "combusted O_2" to atmosphere

Inferring CO_2 Uptake Based on $\Delta(O_2)$



Land Uptake Returns "combusted O_2" to the atmosphere, via photosynthesis:
$6\ CO_2 + H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

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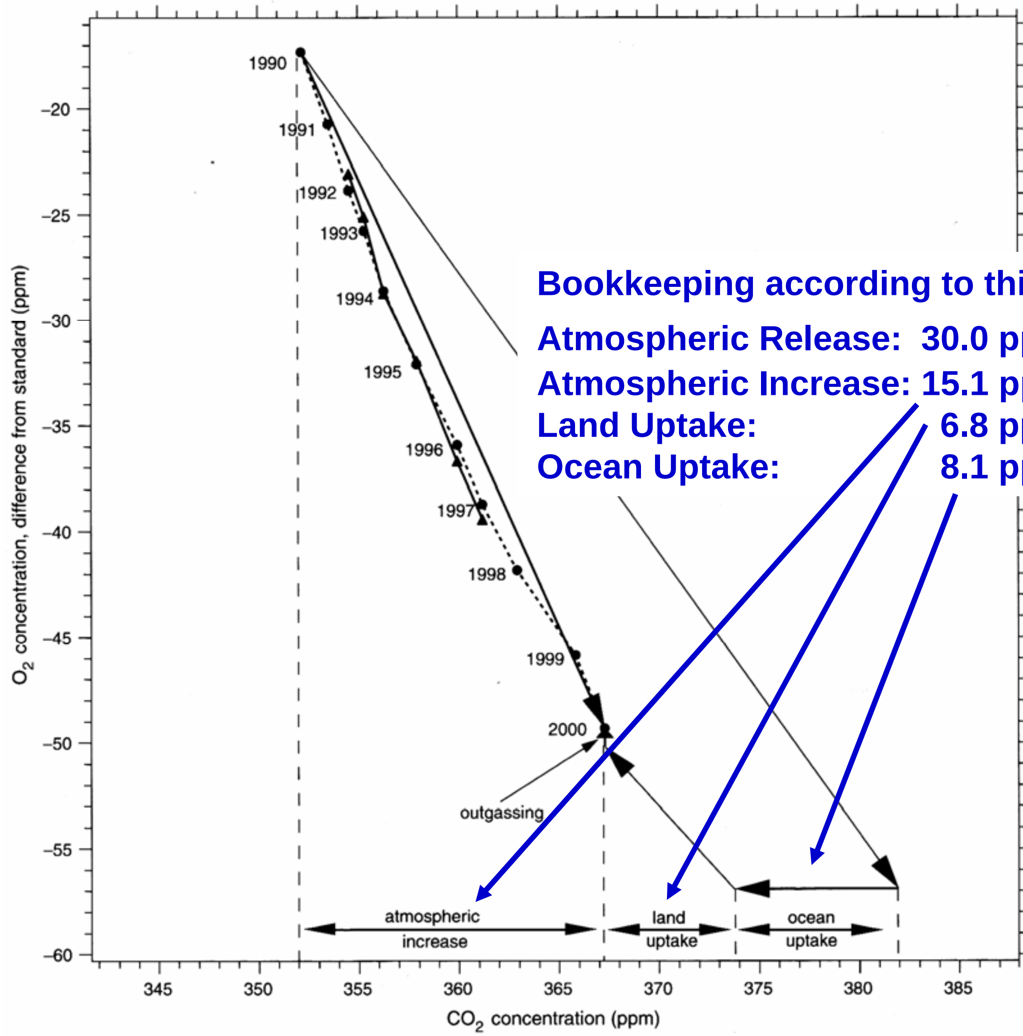

Bookkeeping according to this study:

Atmospheric Release: 30.0 ppm (66 Gt)
Atmospheric Increase: 15.1 ppm (~50% airborne fraction)
Land Uptake: 6.8 ppm (46% of uptake)
Ocean Uptake: 8.1 ppm (54% of uptake)

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Carbon Water Chemistry

Acidity of pure water is 7. This means $[H^+] = 10^{-7}$ moles/liter or 10^{-7} M.

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$$[CO_2(aq)] = H_{CO2}\ p_{CO2} = 3.4 \times 10^{-2}\ \text{M / atm}\ p_{CO2}$$

For CO_2 = 380 ppm:

$$[CO_2(aq)] = 3.4 \times 10^{-2}\ \text{M / atm}\ 380 \times 10^{-2}\ \text{atm} = 1.292 \times 10^{-2}$$

First equilibrium between CO_2, HCO_3^- (bicarbonate), and H^+

$$CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+$$

$$K_1 = \frac{[HCO_3^-]\,[H^+]}{[CO_2(aq)]} = 4.3 \times 10^{-7}\ \text{M (at 298 K)}$$

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Second equilibrium between CO_3^{2-} (carbonate), HCO_3^-, and H^+

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$$

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 4.7 \times 10^{-11} \text{ M (at 298 K)}$$

Carbon Water Chemistry

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$$K_2 = \frac{[CO_3^{2-}]\,[H^+]}{[HCO_3^-]} = 4.7 \times 10^{-11}\ M\ (at\ 298\ K)$$

Can show (see extra slides) that **pH = 5.6** (for CO_2=380 ppm, T=298 K)

Ocean Acidity

Acidity of actual ocean is more complex

Dominant cations are Na^+, K^+, Mg^{2+} and Ca^{2+}

Most common anions are Cl^-, Br^-, and SO_4^{2-}

Positive charge of cations slightly larger than negative charge of anions:

slight difference is called "Ocean Alkalinity", and is balanced by HCO_3^- and CO_3^{2-}

$$\mathbf{[Alk] = [HCO_3^-] + 2\,[CO_3^{2-}]}$$

Atmospheric CO_2, $CO_2(aq)$, HCO_3^-, CO_3^{2-} follow same relations described above.

We define:

$$\mathbf{\Sigma\,[CO_2] = [CO_2(aq)] + [HCO_3^-] + 2\,[CO_3^{2-}]}$$

and note that the relation between $\Sigma\,[CO_2]$ and its components depends on T, Alk, and p_{CO2}

Ocean Acidity

When CO_2 dissolves:

Net: $\mathbf{CO_2(aq) + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^-}$

Remember:

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 4.7 \times 10^{-11}\ \text{M (at 298 K)}$$

If $[HCO_3^-]$ rises, as it must, and CO_3^{2-} falls, as it must, then [H+] must ***RISE*** to maintain the constant value of the above expression !

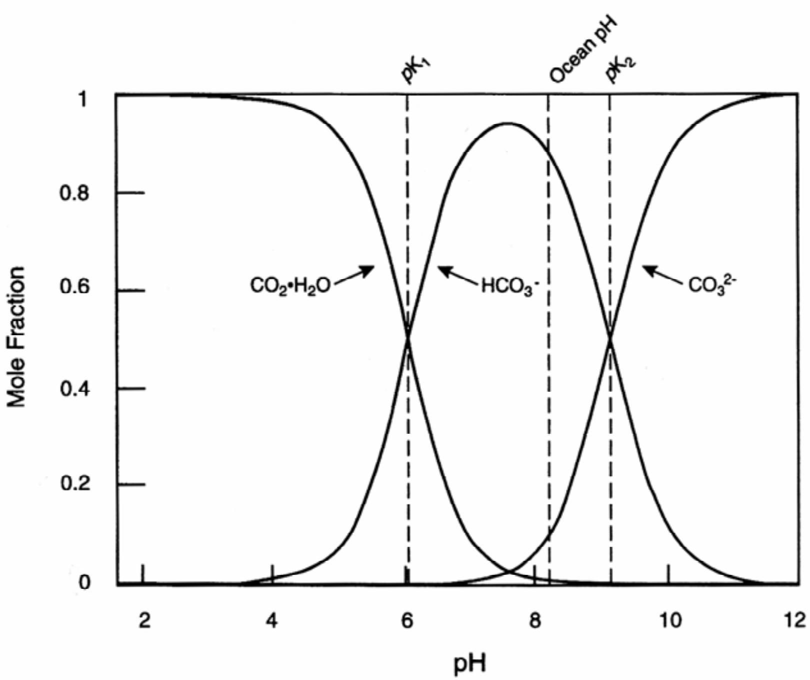

Fig. 6-7 Speciation of total carbonate CO_2(aq) in seawater versus pH.

Jacob, *Introduction to Atmospheric Chemistry*

Ocean Acidity

- Fate of carbon is important:
  - Ocean sink: leads to ocean acidification

Essentially, the ability of the ocean to absorb CO_2 is limited by CO_3^{2-}:

Atmospheric CO_2	280 ppm Pre-Industrial	560 ppm 2 × Pre-Indus.	840 ppm 3 × Pre-Indus.
$[\Sigma\ CO_2]$	1893×10^{-6} M	2040×10^{-6} M	2155×10^{-6} M
$[HCO_3^-]$	1617×10^{-6} M	1850×10^{-6} M	2014×10^{-6} M
$[CO_2\ (aq)]$	8×10^{-6} M	15×10^{-6} M	26×10^{-6} M
$[CO_3^{2-}]$	268×10^{-6} M	176×10^{-6} M	115×10^{-6} M
pH	8.15	7.91	7.76

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Note : due to presence of cations, ocean is slightly basic

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Note : [CO_3^{2-}] drops as atmospheric CO_2 rises

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pH	8.15	7.91	7.76

$$\text{Revelle Factor} = \frac{\Delta p_{CO2}/p_{CO2}}{\Delta\Sigma CO_2/\Sigma CO_2} = \frac{280/420}{147/1966.5} = 8.9 \text{ (from pre-industrial to } 2\times CO_2\text{)}$$

$$= \frac{280/700}{115/2097.5} = 7.3 \text{ (from } 2\times CO_2 \text{ to } 3\times CO_2\text{)}$$

Roger Revelle

In 1957, Revelle co-authored a paper with Hans Suess that suggested that the Earth's oceans would absorb excess carbon dioxide generated by humanity at a much slower rate than previously predicted by geoscientists, thereby suggesting that human gas emissions might create a "greenhouse effect" that would cause global warming over time.[1] Although other articles in the same journal discussed carbon dioxide levels, the Suess-Revelle paper was "the only one of the three to stress the growing quantity of CO_2 contributed by our burning of fossil fuel, and to call attention to the fact that it might cause global warming over time."[2]

Revelle and Suess described the "buffer factor", now known as the "Revelle factor", which is a resistance to atmospheric carbon dioxide being absorbed by the ocean surface layer posed by bicarbonate chemistry. Essentially, in order to enter the ocean, carbon dioxide gas has to partition into one of the components of carbonic acid: carbonate ion, bicarbonate ion, or protonated carbonic acid, and the product of these many chemical dissociation constants factors into a kind of back-pressure that limits how fast the carbon dioxide can enter the surface ocean. This amounted to one of the earliest examples of "integrated assessment", which 50 years later became an entire branch of global warming science.

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

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Al Gore mentions Roger Revelle as a personal inspiration in a segment of the Academy Award-winning global-warming documentary "An Inconvenient Truth."

Also, this Revelle factor is specifically what Houghton is referring to at the end of the second full paragraph on page 34 of the reading.

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

Ocean Uptake

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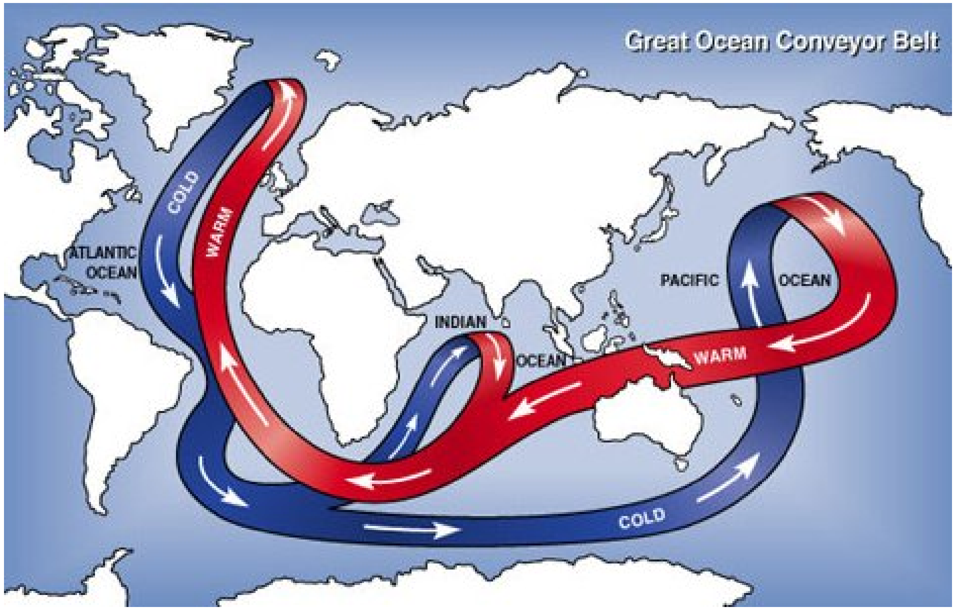
b) Detrital material "rains" from surface to deep waters, contributing to higher CO_2 in intermediate and deep waters



http://science.nasa.gov/headlines/y2004/05mar_arctic.htm

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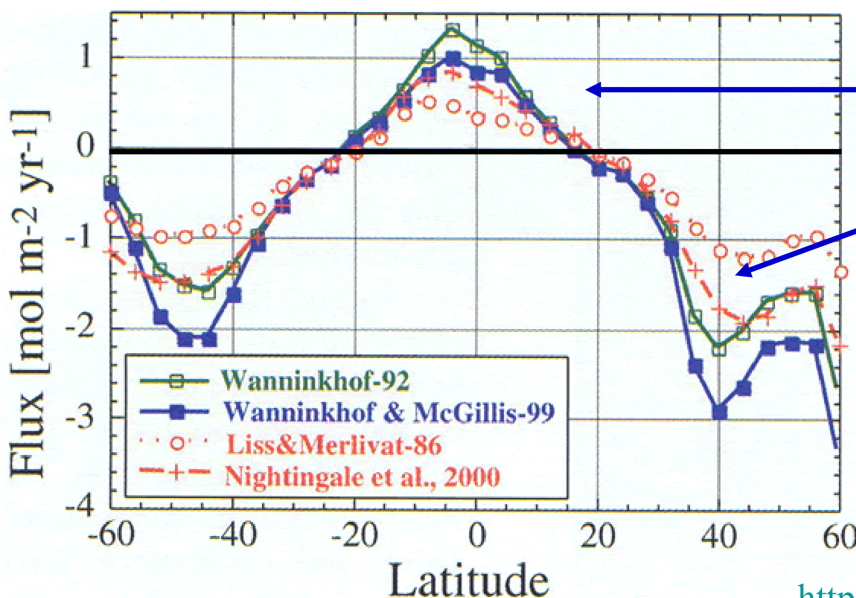


CO_2 comes out of tropical ocean

CO_2 goes into rest of the ocean

http://www.pmel.noaa.gov/pubs/outstand/feel2331/images/fig05.gif

Fate of Carbon Important

Land sink

As CO_2 ↑, photosynthesis (all things being equal) will increase.

Known as the **"CO_2 fertilizer" effect**

Difficult to quantify: plants behave differently as individuals than in groups

The carbon dioxide 'fertilisation' effect

An important positive effect of increased carbon dioxide (CO_2) concentrations in the atmosphere is the boost to growth in plants given by the additional CO_2. Higher CO_2 concentrations stimulate photosynthesis, enabling the plants to fix carbon at a higher rate. This is why in glasshouses additional CO_2 may be introduced artificially to increase productivity. The effect is particularly applicable to what are called C3 plants (such as wheat, rice and soya bean), but less so to C4 plants (for example, maize, sorghum, sugar-cane, millet and many pasture and forage grasses). Under ideal conditions it can be a large effect; for C3 crops under doubled CO_2, an average of +30%.[37] However, under real conditions on the large scale where water and nutrient availability are also important factors influencing plant growth, experiments show that the increases, although difficult to measure accurately, tend to be substantially less than the ideal.[38] In experimental work, grain and forage quality declines with CO_2 enrichment and higher temperatures. More research is required especially for many tropical crop species and for crops grown under suboptimal conditions (low nutrients, weeds, pests and diseases).

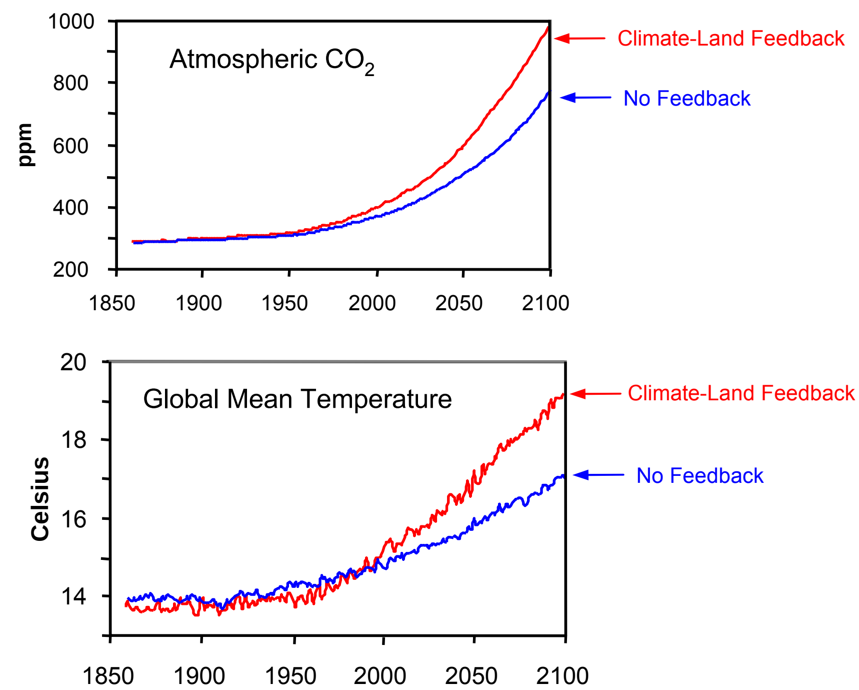
Page 166, Houghton

Fate of Carbon Important

Land sink: relatively short lived reservoir !!!

- In this model, future water stress due to climate change eventually limits plant growth
- IPCC 2007 did not consider carbon cycle feedbacks in latest assessment, as there is no scientific consensus on the direction (much less magnitude) of this effect
- The results of this model were the basis for Fig 3.5 of the Houghton reading

Projected future CO_2 and T for a single CO_2 emission scenario ⇒



Cox et al., *Nature*, 2000

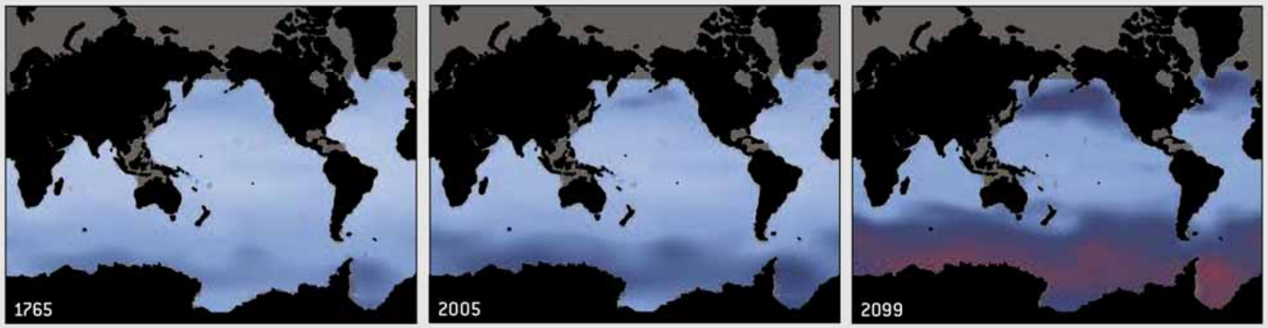
Fate of Carbon Important

Ocean uptake leads to ocean acidification:

Bad news for ocean dwelling organisms that precipitate shells (basic materials)

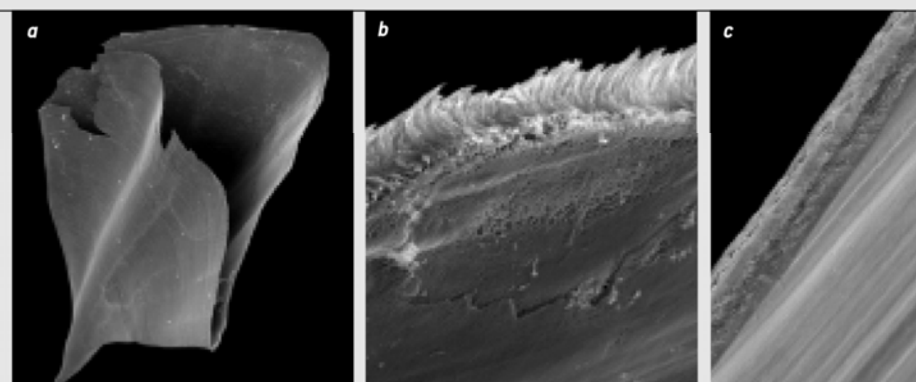
THE (RAGGED) FUTURE OF ARAGONITE

Diminishing pH levels will weaken the ability of certain marine organisms to build their hard parts and will be felt soonest and most severely by those creatures that make those parts of aragonite, the form of calcium carbonate that is most prone to dissolution. The degree of threat will vary regionally.



Before the Industrial Revolution (*left*), most surface waters were substantially "oversaturated" with respect to aragonite (*light blue*), allowing marine organisms to form this mineral readily. But now (*center*), polar surface waters are only marginally oversaturated (*dark blue*). At the end of this century (*right*), such chilly waters, particularly those surrounding Antarctica, are expected to become undersaturated (*purple*), making it difficult for organisms to make aragonite and causing aragonite already formed to dissolve.

Pteropods form a key link in the food chain throughout the Southern Ocean. For these animals (and creatures that depend on them), the coming changes may be disastrous, as the images at the right suggest. The shell of a pteropod kept for 48 hours in water undersaturated with respect to aragonite shows corrosion on the surface (*a*), seen most clearly at high magnification (*b*). The shell of a normal pteropod shows no dissolution (*c*).



Doney, The Dangers of Ocean Acidification, *Scientific American*, March, 2006

CO_2 Latitudinal Gradient: “Fingerprint” of Human Release

Observational Constraints on the Global Atmospheric CO_2 Budget

PIETER P. TANS, INEZ Y. FUNG, TARO TAKAHASHI

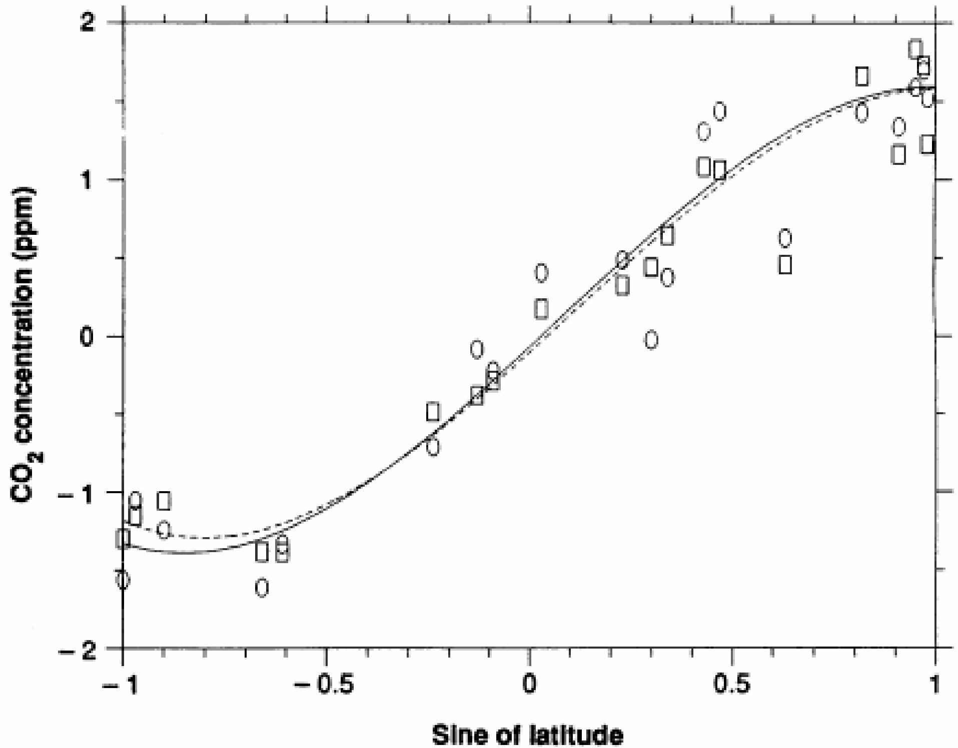
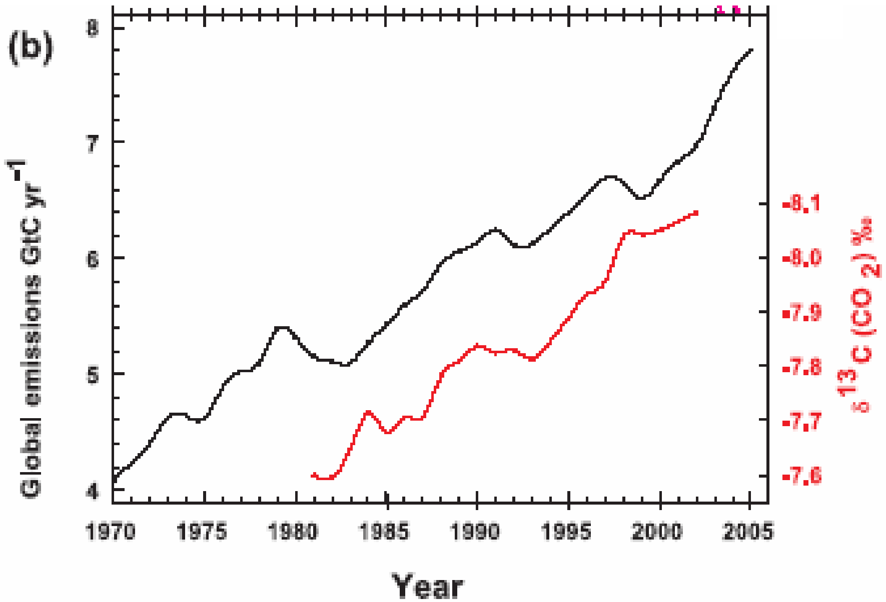


Fig. 5. Results of model calculations (scenario 1, Table 3) of the atmospheric CO_2 concentrations at the GMCC sites (squares and dashed curve) are compared with the observed concentrations (circles and solid curve). All values are relative to the global mean. The curves are least-squares cubic polynomial fits; the differences between the curves are not statistically significant.

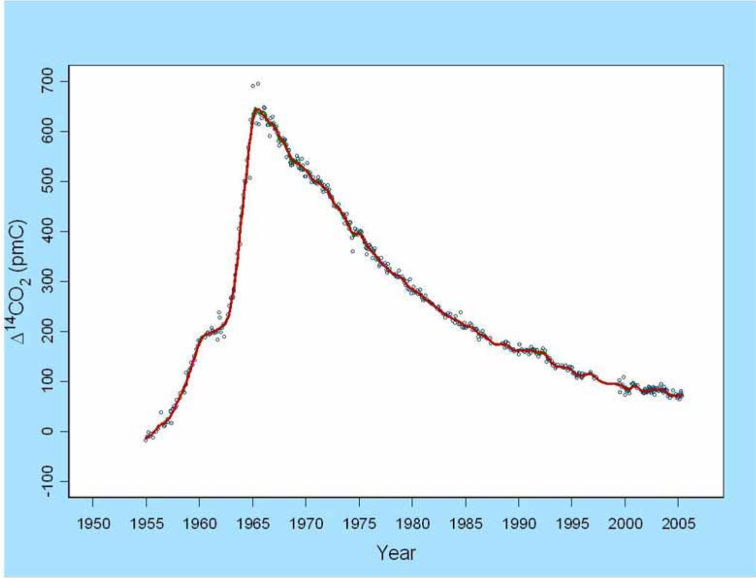
SCIENCE, VOL. 247
1990

$^{13}CO_2$ Time Evolution: "Fingerprint" of Fossil Fuel Burning



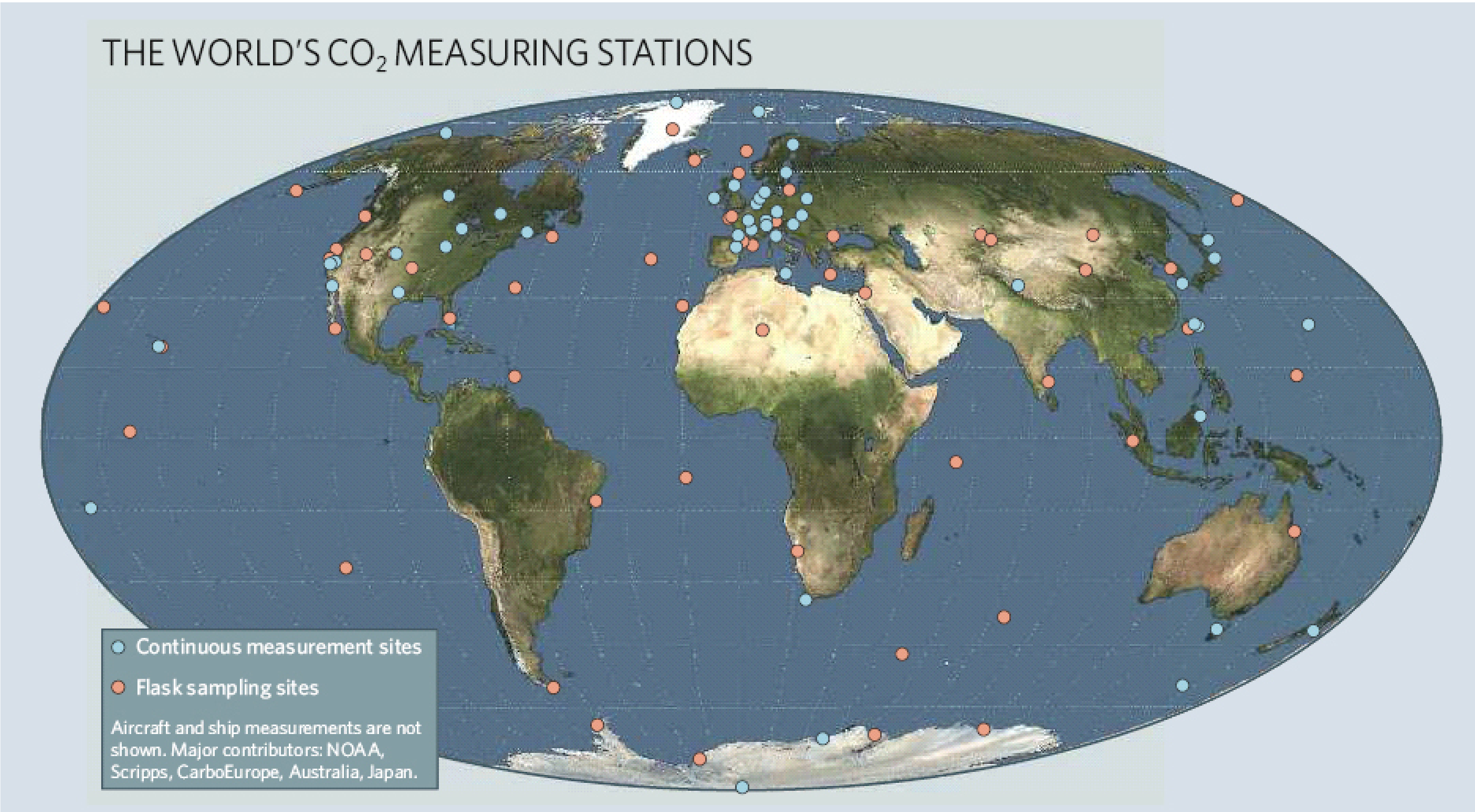
Chapter 2, *IPCC 2007*

$^{14}CO_2$ has "fingerprint" of something else:



http://www.niwa.cri.nz/__data/assets/image/0018/43452/Bhd_14co2_800.jpg

Carbon Sinks Hard to Specify Because CO_2 Monitoring Network is Sparse

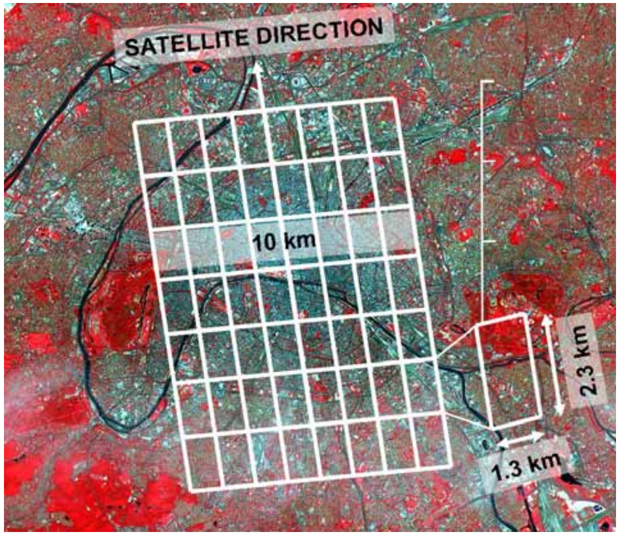


Nature, *450*, 789-790, 5 Dec 2007.

Orbiting Carbon Observatory (OCO) Mission

http://oco.jpl.nasa.gov

- **First global measurements of CO_2 (500,000 measurements per day)**



- **Will quantify geographic distribution of *Carbon Fluxes***

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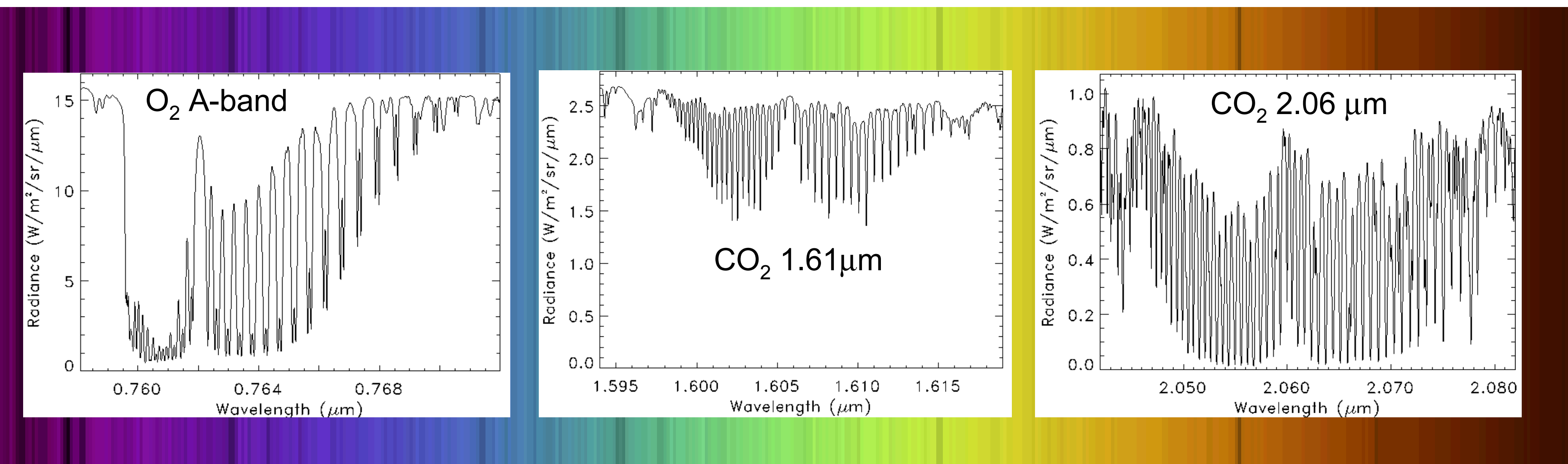

- **Records very high resolution spectra of reflected solar radiation**
- **Launch planned for early 2009**

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I am a founding member of the OCO Science Team and plan to fly out to Vandenberg AFB (near Santa Barbara, Calif) on Sat, 21 Feb

Tim will present class on Feb 24 ☺

Instrument "first light" no sooner than 1 April 2009 (nice choice of date!)
Once first light is received, I will be spending a lot of time in Calif

Can follow launch activities at:

http://www.vandenberg.af.mil/
http://www.nasa.gov/mission_pages/oco/launch/launch_blog.html

I may set up my own blog. If so, will email class the URL

Extra Slides

Carbon Water Chemistry

Acidity of pure water is 7. This means $[H^+] = 10^{-7}$ moles/liter or 10^{-7} M.

What is acidity of water in equilibrium with atmospheric CO_2 ?

$$[CO_2(aq)] = H_{CO2}\ p_{CO2} = 3.4 \times 10^{-2}\ \text{M / atm}\ p_{CO2}$$

For CO_2 = 380 ppm:

$$[CO_2(aq)] = 3.4 \times 10^{-2}\ \text{M / atm}\ 380 \times 10^{-2}\ \text{atm} = 1.292 \times 10^{-2}$$

First equilibrium between CO_2, HCO_3^- (bicarbonate), and H^+

$$CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+$$

$$K_1 = \frac{[HCO_3^-]\,[H^+]}{[CO_2(aq)]} = 4.3 \times 10^{-7}\ \text{M (at 298 K)}$$

Second equilibrium between CO_3^{2-} (carbonate), HCO_3^-, and H^+

$$K_2 = \frac{[CO_3^{2-}]\,[H^+]}{[HCO_3^-]} = 4.7 \times 10^{-11}\ \text{M (at 298 K)}$$

Carbon Water Chemistry

Acidity of pure water is 7. What is acidity of water in equilibrium with atmospheric CO_2 ?

It can be shown (see, for example, page 294 of Seinfeld and Pandis, *Atmospheric Chemistry and Physics*, 2006):

$$[H^+]^3 - (K_w + H_{CO2}K_1p_{CO2})[H^+] - 2\ H_{CO2}K_1K_2\ p_{CO2} = 0$$

where $K_w = [H^+][OH^-] = 10^{-14}\ M^2$ at 298 K

This equation can be solved for $[H^+]$ and hence pH

Carbon Water Chemistry

Acidity of pure water is 7. What is acidity of water in equilibrium with atmospheric CO_2 ?

Shortcut:

$[CO_2(aq)] = H_{CO2}\ p_{CO2} = 3.4 \times 10^{-2}$ M / atm $p_{CO2} = 1.292 \times 10^{-5}$ M for present day atmosphere

$[H^+]\,[HCO_3^-] = K_1\,[CO_2(aq)] = 4.3 \times 10^{-7}\ M \times 1.292 \times 10^{-5}\ M = 5.56 \times 10^{-12}\ M^2$

Assume charge balance is primarily between $[H^+]$ and $[HCO_3^-]$:

i.e., that $[H^+] = [HCO_3^-]$ both of which are >> $[CO_3^{2-}]$

$[H^+]\,[H^+] = 5.56 \times 10^{-12}\ M^2 \Rightarrow [H^+] = 2.357 \times 10^{-6}$ M

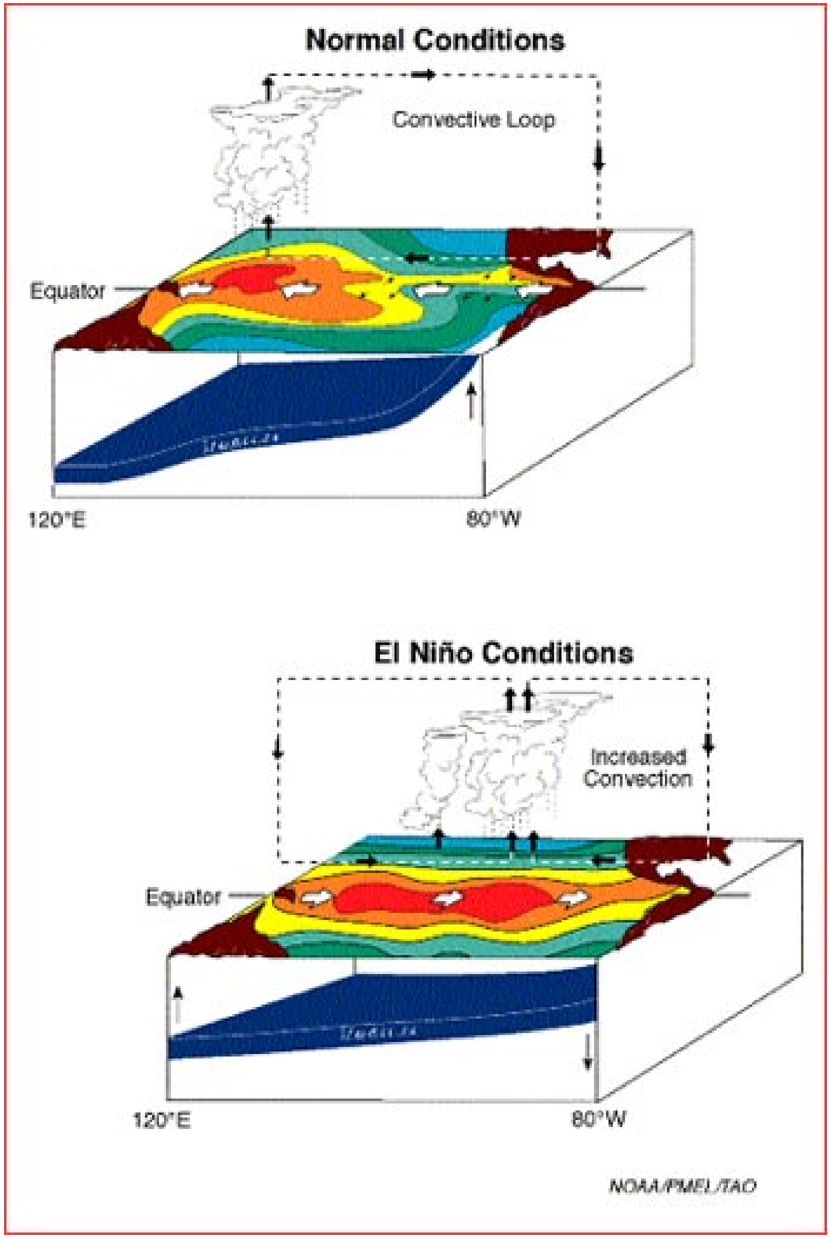
pH = 5.6 (380 ppm, 298 K)

Is our assumption justified? :

$[CO_3^{2-}] = K_2\,[HCO_3^-] / [H^+] \approx 4.7 \times 10^{-11}$ M

If $[H^+] = [HCO_3^-]$, then both of which indeed are >> $[CO_3^{2-}]$

Ocean Circulation: El Niño



Between normal conditions, the trade winds blow towards the west across the tropical Pacific. Cool waters from the deep ocean, rich in nutrients, upwell along the western coast of South America. Major convection occurs around Indonesia.

During El Niño, the warm pool of water in the Tropical Western Pacific "collapses", flowing to the east. The convection cell moves to the east, changing weather around the globe. The collapse of the TWP warm pool shuts off tropical upwelling, which devastates the fishing industry throughout South America (no nutrients from upwelling, no fish!) and also greatly reduces the normal release of CO_2 to the atmosphere from deep waters rich in ΣCO_2.

http://whyfiles.org/050el_nino/index.php?g=2.txt

Ocean Uptake

– Solubility Pump:

a) more CO_2 can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO_2

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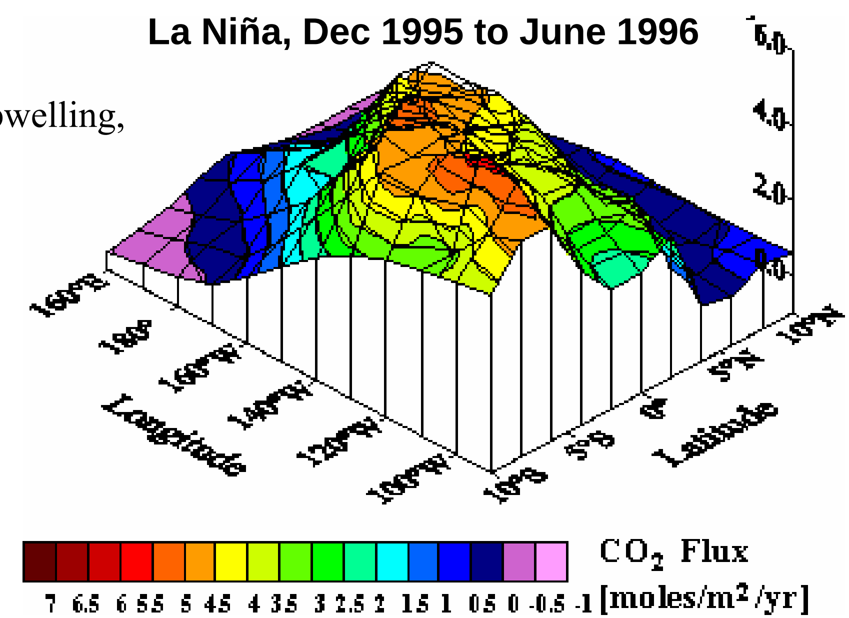
a) Ocean biology limited by availability of nutrients such as NO_3^-, PO_4^-, and Iron. Not carbon limited.

b) Detrital material "rains" from surface to deep waters, contributing to higher CO_2 in intermediate and deep waters

The equatorial Pacific, a region of strong upwelling, is normally source of atmospheric CO_2 (high levels of ΣCO_2 in these waters)



http://www.pmel.noaa.gov/co2/elnino.html

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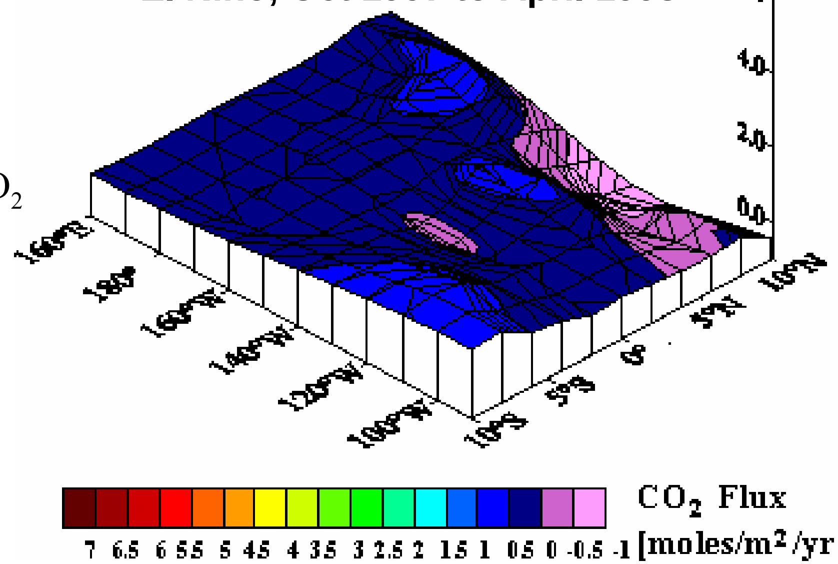
Equatorial Pacific upwelling is "capped" during El Niño. This source of atmospheric CO_2 is shut-down, which should, ***all other things being equal***, lead to a reduction in atmospheric CO_2

El Niño, Oct 1997 to April 1998



http://www.pmel.noaa.gov/co2/elnino.html

Indonesia Wildfires Associated With 1997 El Niño

Of course, rarely are ***"all other things equal"*** :

The amount of carbon released from peat and forest fires in Indonesia during 1997

Susan E. Page*, Florian Siegert†‡, John O. Rieley§, Hans-Dieter V. Boehm‡, Adi Jaya|| & Suwido Limin||

* *Department of Geography, University of Leicester, Leicester LE1 7RH, UK*

widespread fires throughout the forested peatlands of Indonesia[7–10] during the 1997 El Niño event. Here, using satellite images of a 2.5 million hectare study area in Central Kalimantan, Borneo, from before and after the 1997 fires, we calculate that 32% (0.79 Mha) of the area had burned, of which peatland accounted for 91.5% (0.73 Mha). Using ground measurements of the burn depth of peat, we estimate that 0.19–0.23 gigatonnes (Gt) of carbon were released to the atmosphere through peat combustion, with a further 0.05 Gt released from burning of the overlying vegetation. Extrapolating these estimates to Indonesia as a whole, we estimate that between 0.81 and 2.57 Gt of carbon were released to the atmosphere in 1997 as a result of burning peat and vegetation in Indonesia. This is equivalent to 13–40% of the mean annual global carbon emissions from fossil fuels, and contributed greatly to the largest annual increase in atmospheric CO_2 concentration detected since records began in 1957 (ref. 1).

NATURE | VOL 420 | 7 NOVEMBER 2002 | www.nature.com/nature