Global Carbon Cycle
AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2015

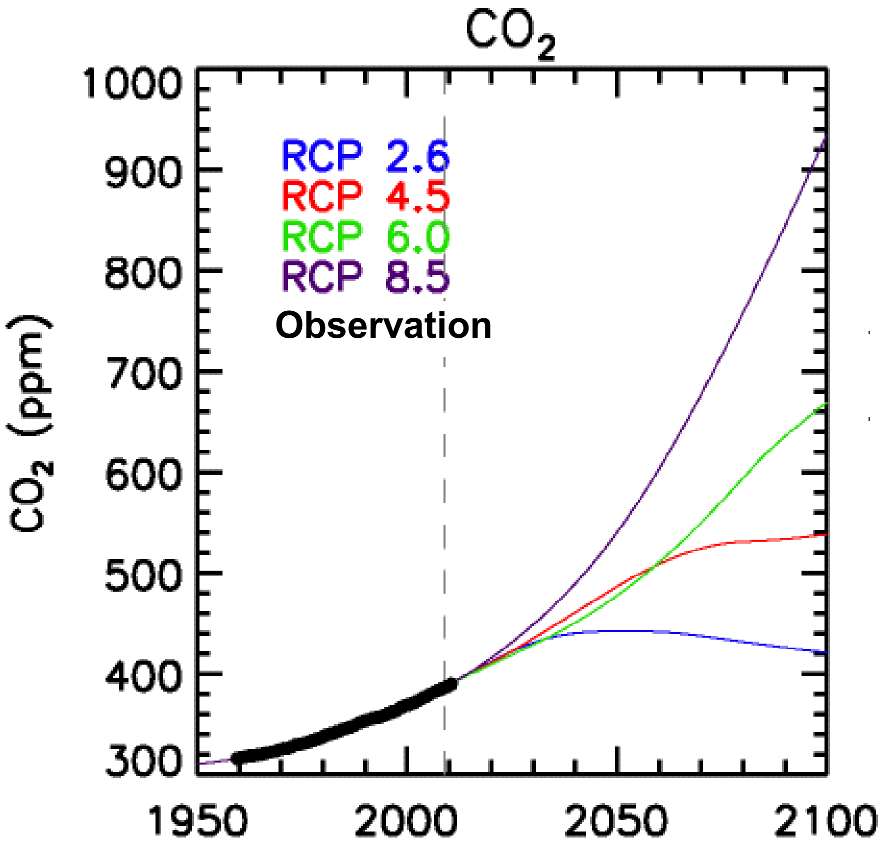
Goals for today:

- **Overview of the Global Carbon Cycle, "scratching below the surface" of the reading material**
- **Ocean and land uptake of CO_2**
- **Connect to recent news, prior lecture (glacial CO_2 draw down), as well as IPCC (2013)**

Lecture 5

10 February 2015

Motivation 1



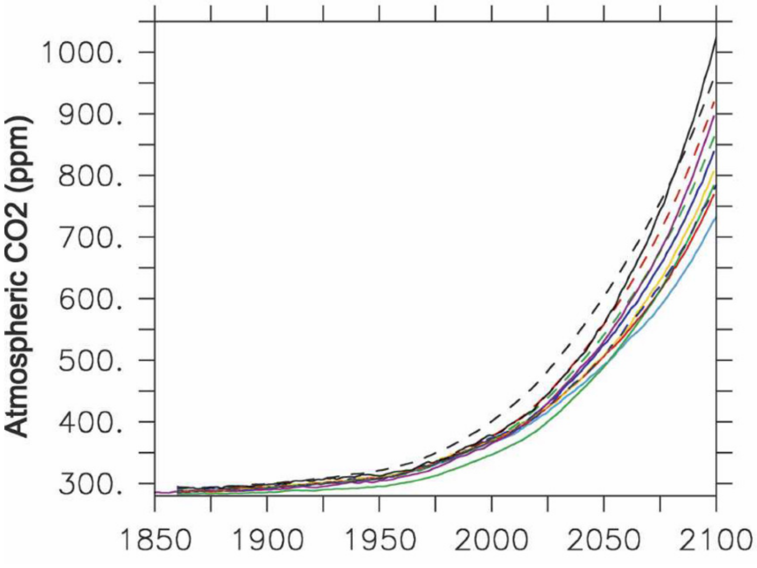
- RCP: Representative Concentration Pathway
  Integer represents W m^{-2} RF of climate that occurs at the end of this century, for each scenario

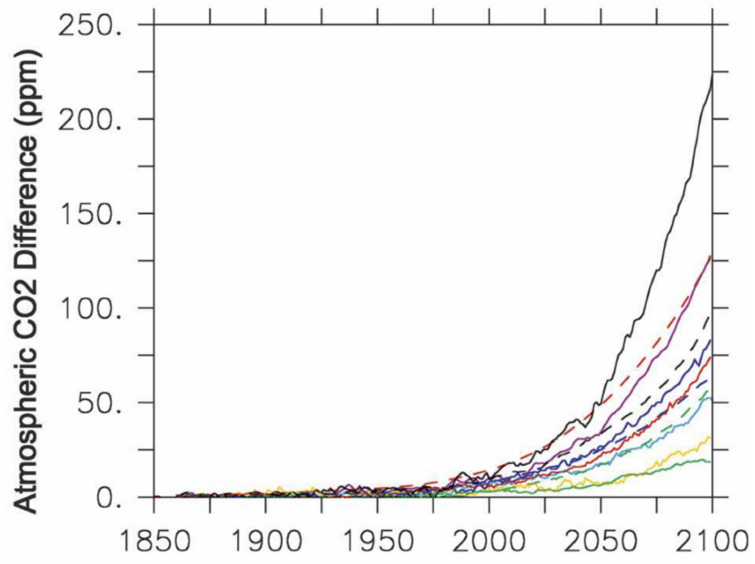
- GHG mixing ratio time series for CO_2, CH_4, N_2O, as well as CFCs, HCFCs, and HFCs provided to climate model groups

- What is the utility of "command central" providing GHG scenarios to the climate model groups?

- How do you think these various scenarios are devised?

Motivation 2





- Prior slide examined atmospheric$CO_{2\ MR}$ from a single model of the global carbon cycle

- Friedlingstein et al. (2006) compared $CO_{2\ MR}$ from **11** different coupled climate-carbon cycle models, each constrained by the *same* specified time series of anthropogenic CO_2 emission and found:

    1) future climate change will reduce the efficiency of the *Earth system* to absorb the anthropogenic carbon perturbation

    2) the difference in $CO_{2\ MR}$ between a run with an interactive carbon-cycle and a run with a non-interactive carbon-cycle varies from 20 to 200 ppm among these **11** models (yikes!)

Motivation 3

KYOTO PROTOCOL TO THE UNITED NATIONS FRAMEWORK CONVENTION ON CLIMATE CHANGE

UNITED NATIONS

1998

Article 3

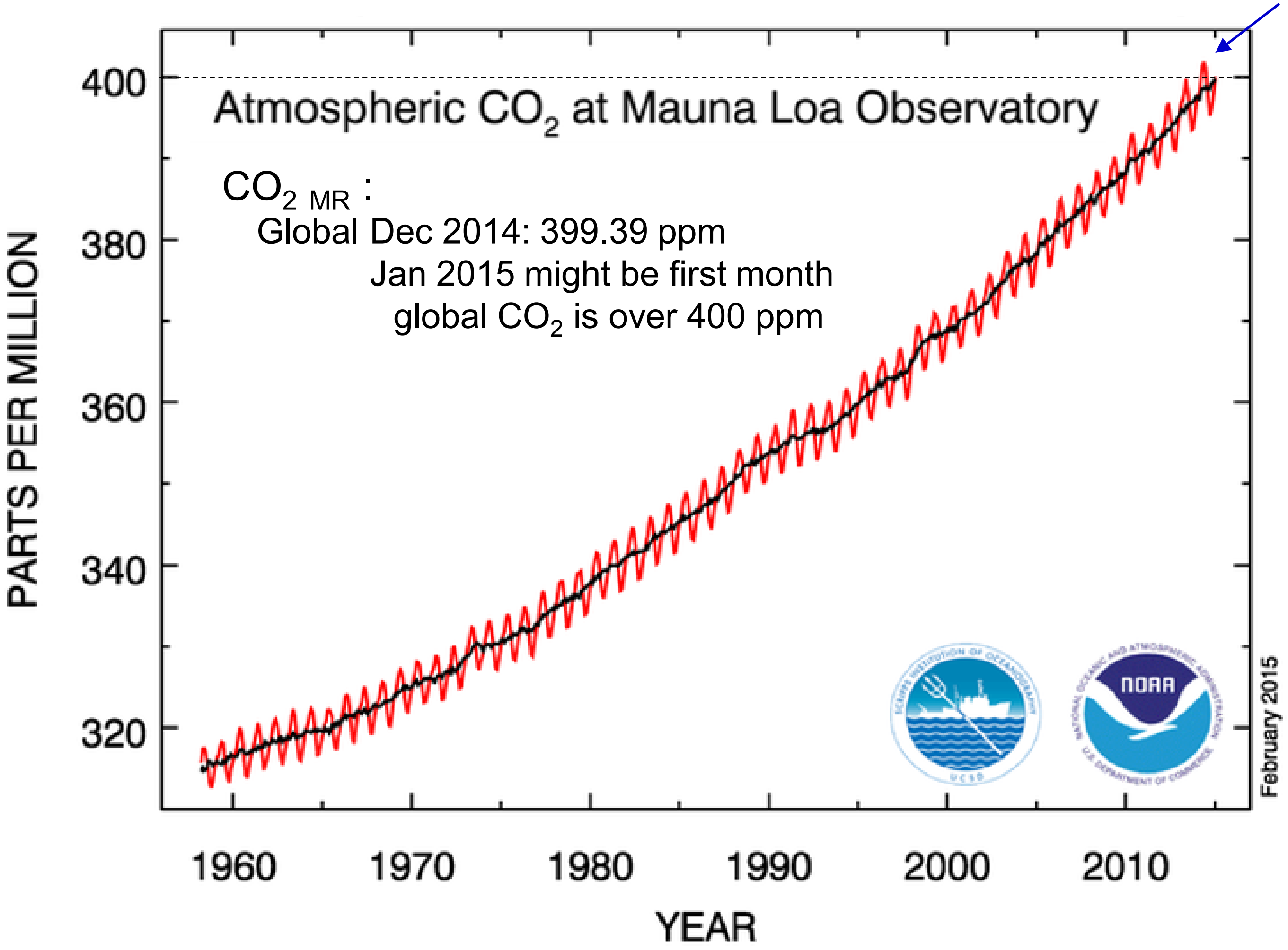
1. The Parties included in Annex I shall, individually or jointly, ensure that their aggregate anthropogenic carbon dioxide equivalent emissions of the greenhouse gases listed in Annex A do not exceed their assigned amounts, calculated pursuant to their quantified emission limitation and reduction commitments inscribed in Annex B and in accordance with the provisions of this Article, with a view to reducing their overall emissions of such gases by at least 5 per cent below 1990 levels in the commitment period 2008 to 2012.

2. Each Party included in Annex I shall, by 2005, have made demonstrable progress in achieving its commitments under this Protocol.

3. The net changes in greenhouse gas emissions by sources and removals by sinks resulting from direct human-induced land-use change and forestry activities, limited to afforestation, reforestation and deforestation since 1990, measured as verifiable changes in carbon stocks in each commitment period, shall be used to meet the commitments under this Article of each Party included in Annex I. The greenhouse gas emissions by sources and removals by sinks associated with those activities shall be reported in a transparent and verifiable manner and reviewed in accordance with Articles 7 and 8.

Modern CO_2 Record

Sustained data above
400 ppm at Mauna Loa Obs (MLO)
starting May 2014

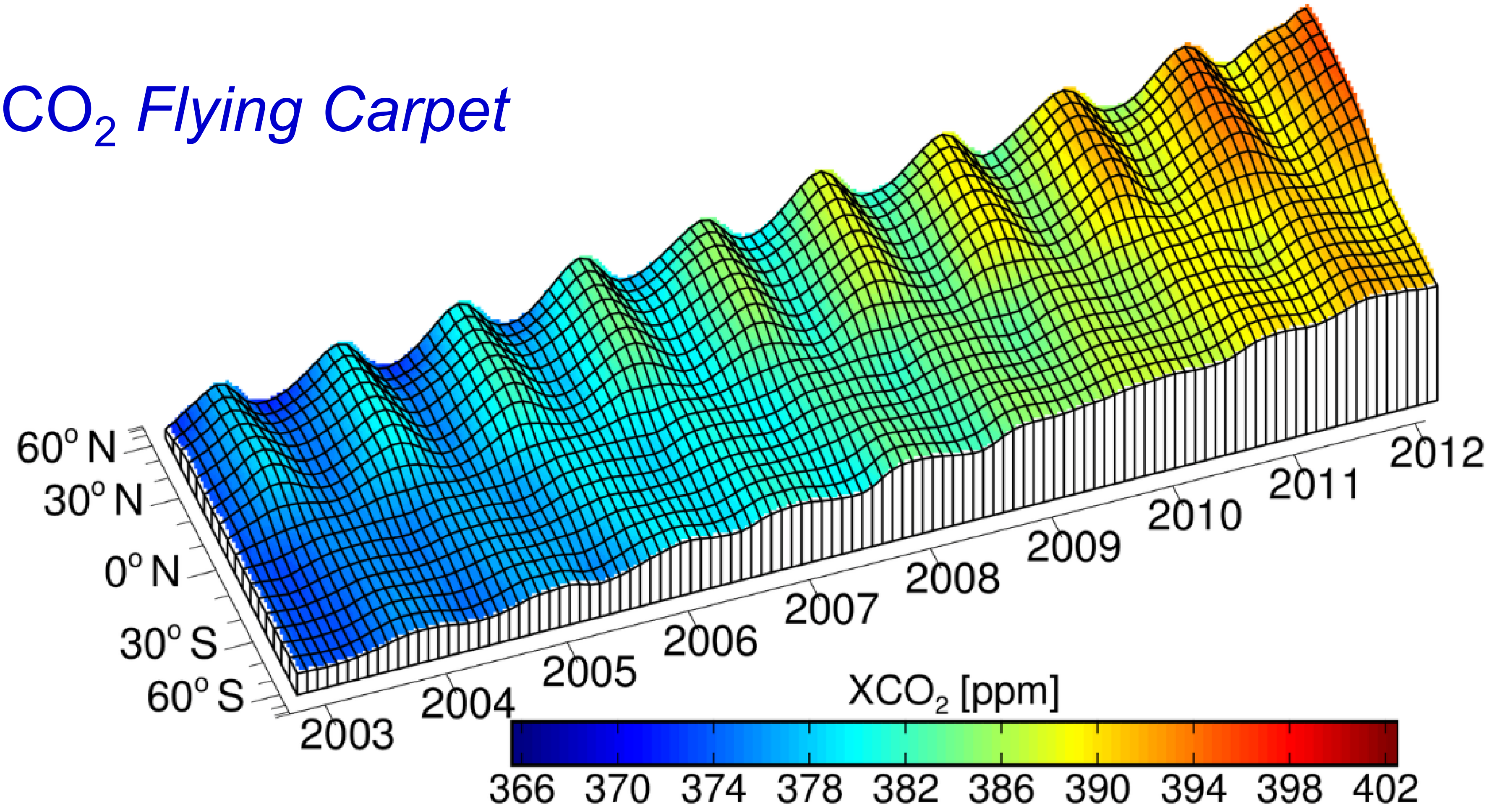


$CO_{2\ MR}$:
Global Dec 2014: 399.39 ppm
Jan 2015 might be first month
global CO_2 is over 400 ppm

Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
http://www.esrl.noaa.gov/gmd/ccgg/trends

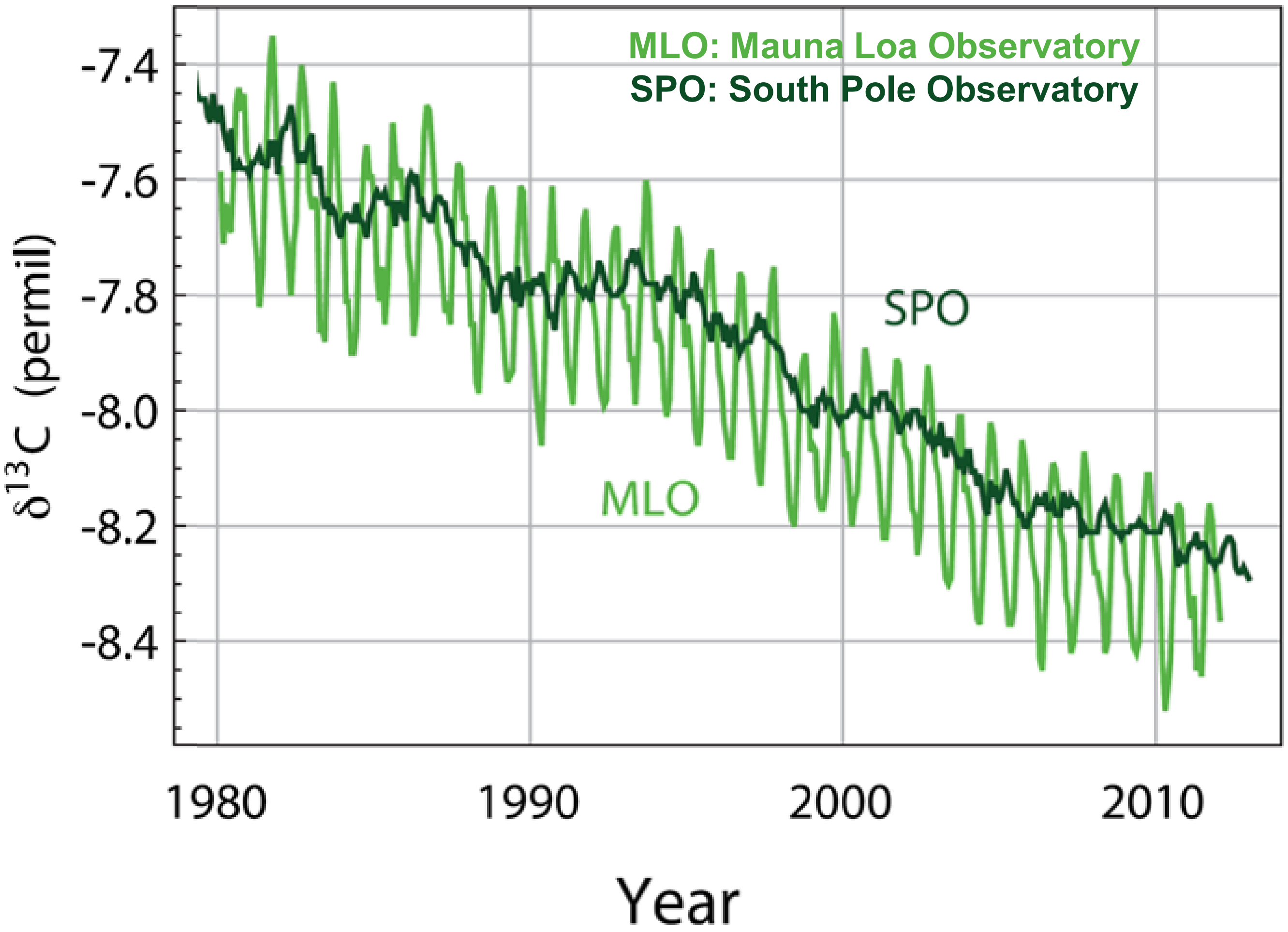
Modern CO_2 Record

CO_2 *Flying Carpet*

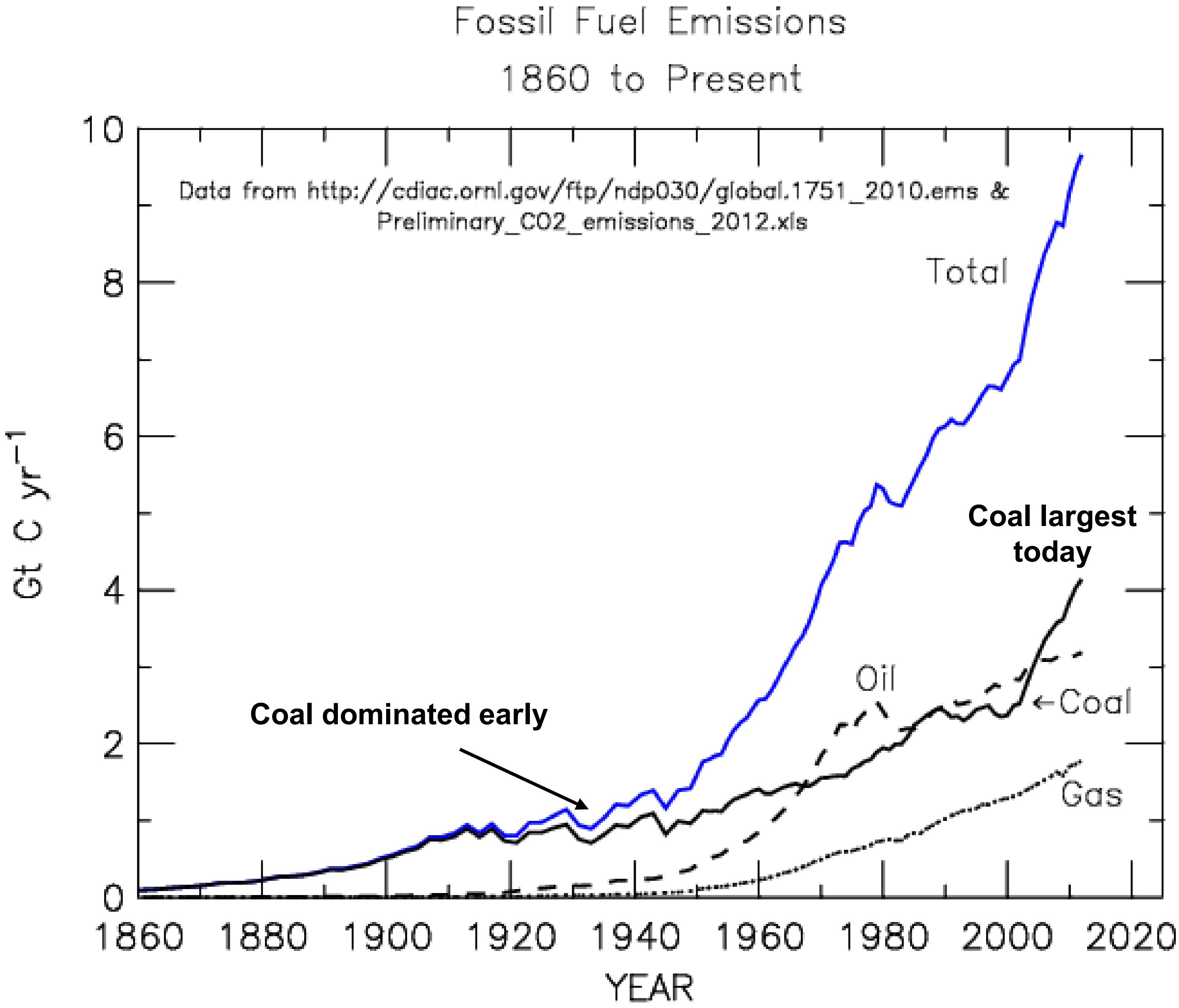


Model simulation constrained by early space-borne observations
http://www.esa-ghg-cci.org/?q=node/115

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



Chapter 6, *IPCC 2013*



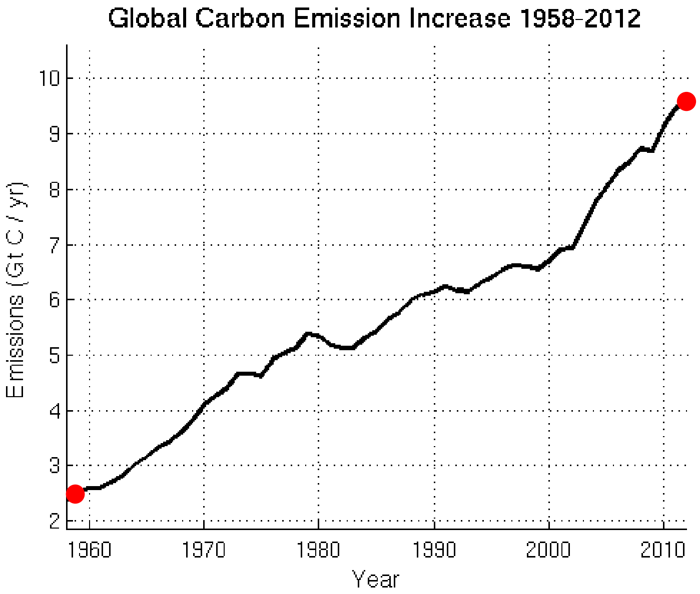
Fossil Fuel Emissions
1860 to Present

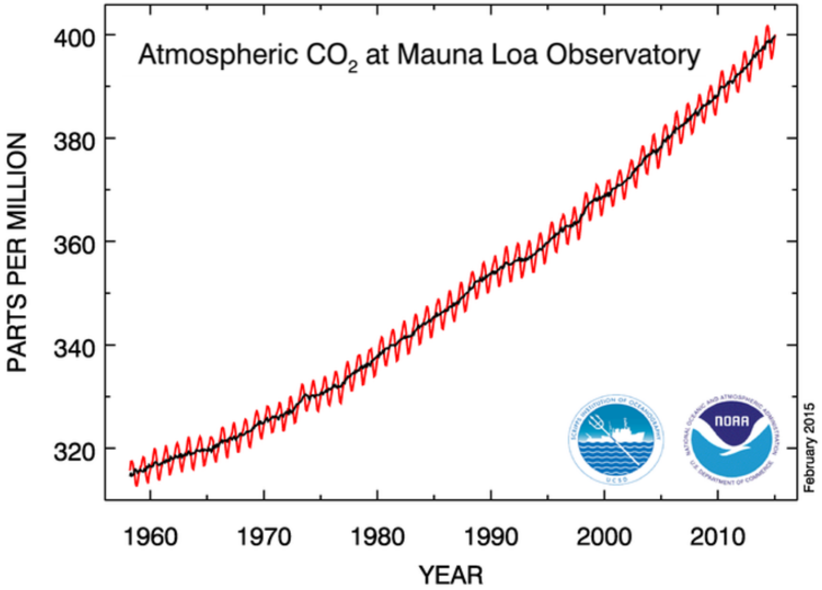
Data from http://cdiac.ornl.gov/ftp/ndp030/global.1751_2010.ems &
Preliminary_CO2_emissions_2012.xls

Coal dominated early

Coal largest today

Fossil Fuel Emissions





Fossil fuel emissions, 1959 = **2.5** Gt C
2012 = **9.7** Gt C

What are the primary driving factors for this rise?

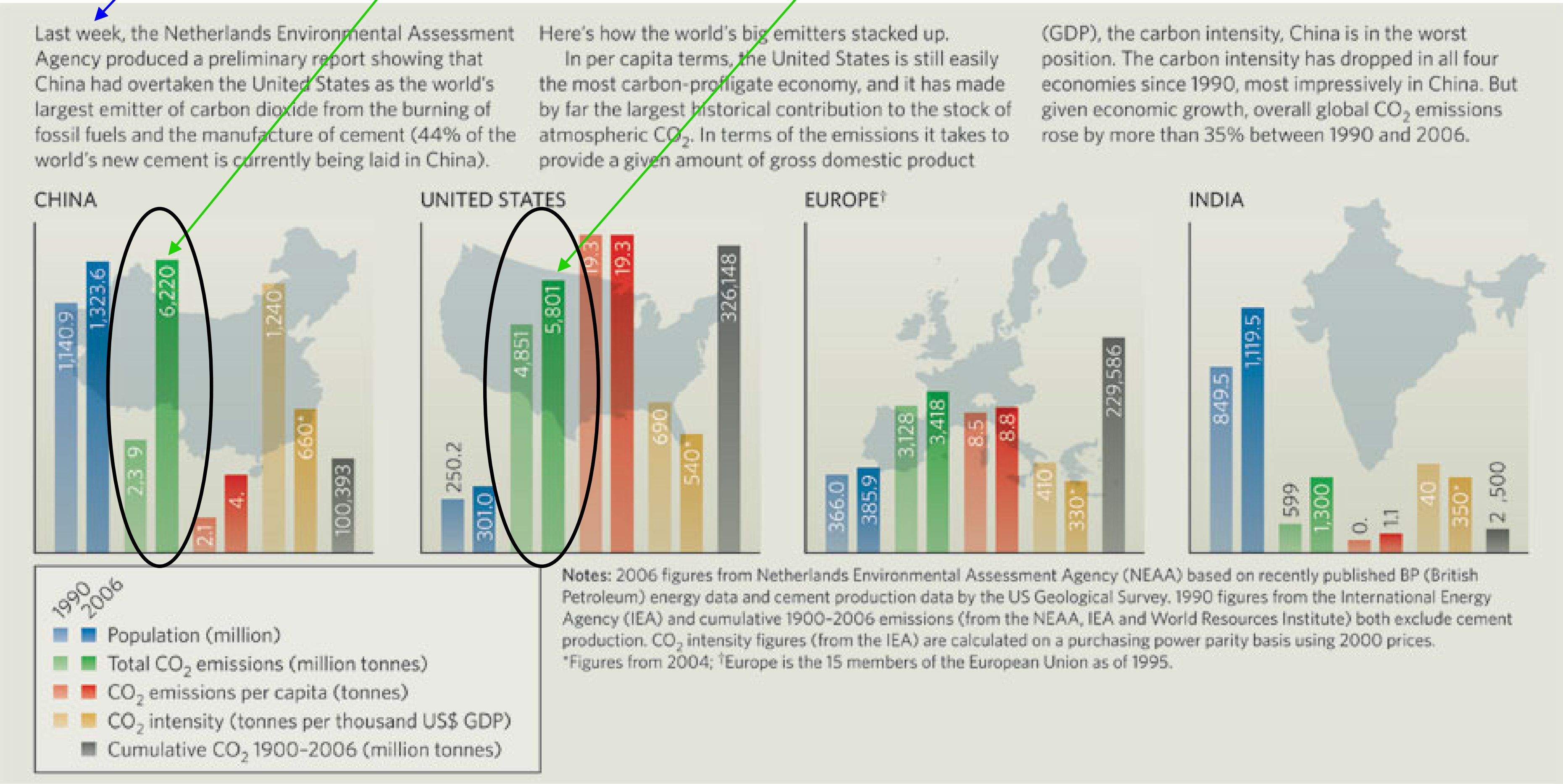
How can we quantify standard of living versus population growth contribution to this rise?

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.

- 🟦 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.

Source: http://www.nature.com/nature/journal/v447/n7148/fig_tab/4471038a_F1.html

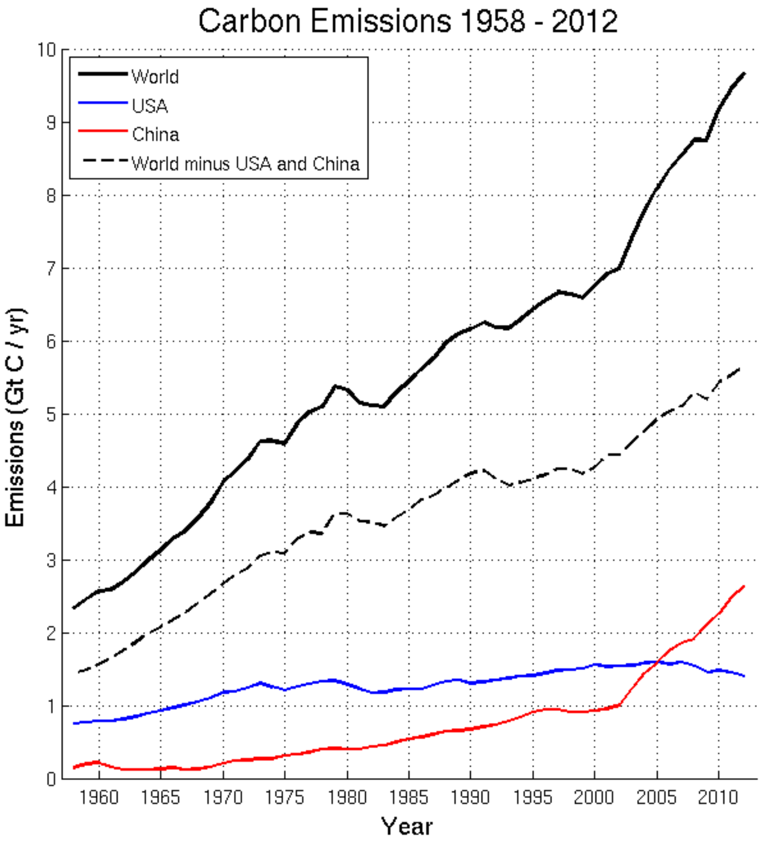
12 Nov 2014

- The Presidents of the United States and China announced their respective post-2020 actions on climate change, recognizing that these actions are part of the longer range effort to transition to low-carbon economies, **mindful of the global temperature goal of 2°C**. The **U.S.** intends to achieve an economy-wide target of **reducing emissions by 26%-28% below its 2005 level in 2025** ; **China** intends to achieve **peaking of CO_2 emissions around 2030** and make best effort to peak early & intends to increase share of non-fossil fuels in primary energy consumption to ~20% by 2030.

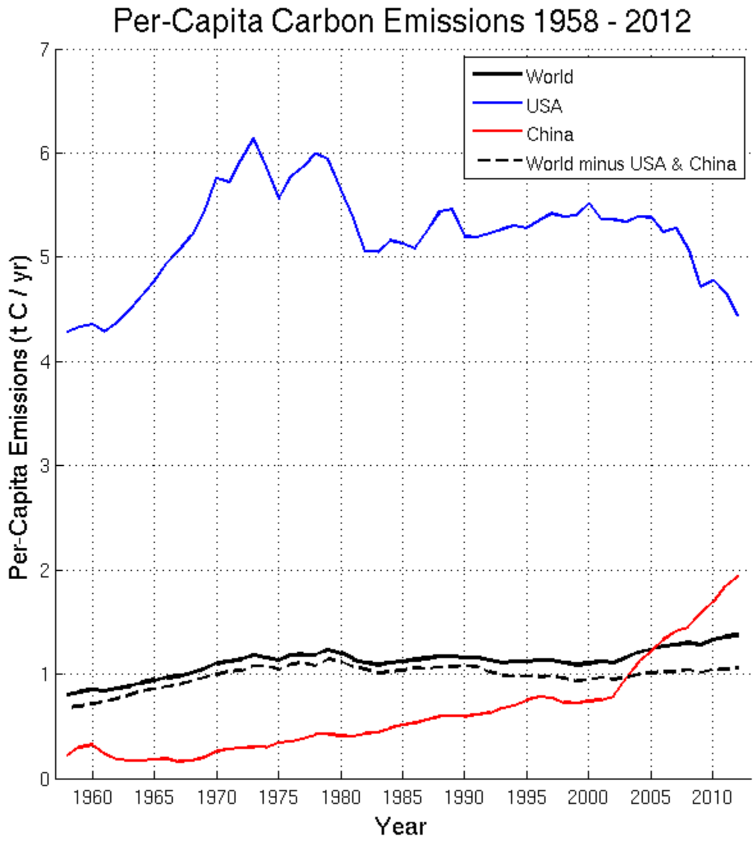
- The United States and China hope that by announcing these targets now, they can inject momentum into the global climate negotiations and inspire other countries to join in coming forward with ambitious actions as soon as possible, preferably by the first quarter of 2015 … to reach a successful global climate agreement in Paris in late 2015.

- The two sides have among other things:
  - established the U.S.-China Climate Change Working Group (CCWG), under which they have launched initiatives on vehicles, smart grids, carbon capture, energy efficiency, GHG data management, forests and industrial boilers;
  - agreed to work together towards the global phase down of **hydrofluorocarbons (HFCs)**
  - created the U.S.-China Clean Energy Research Center, which facilitates collaborative work in carbon capture and storage technologies, energy efficiency in buildings, and clean vehicles; and
  - agreed on a joint peer review of inefficient fossil fuel subsidies under the G-20.

Text: http://www.whitehouse.gov/the-press-office/2014/11/11/us-china-joint-announcement-climate-change
Image: http://www.asianews.it/news-en/China-and-the-United-States-agree-to-climate-agreement-by-2030-32676.html



Carbon Emissions 1958 - 2012



Per-Capita Carbon Emissions 1958 - 2012

Figures courtesy Walt Tribett

Global Per-Capita (PC) Carbon Emissions 1751 - 2012

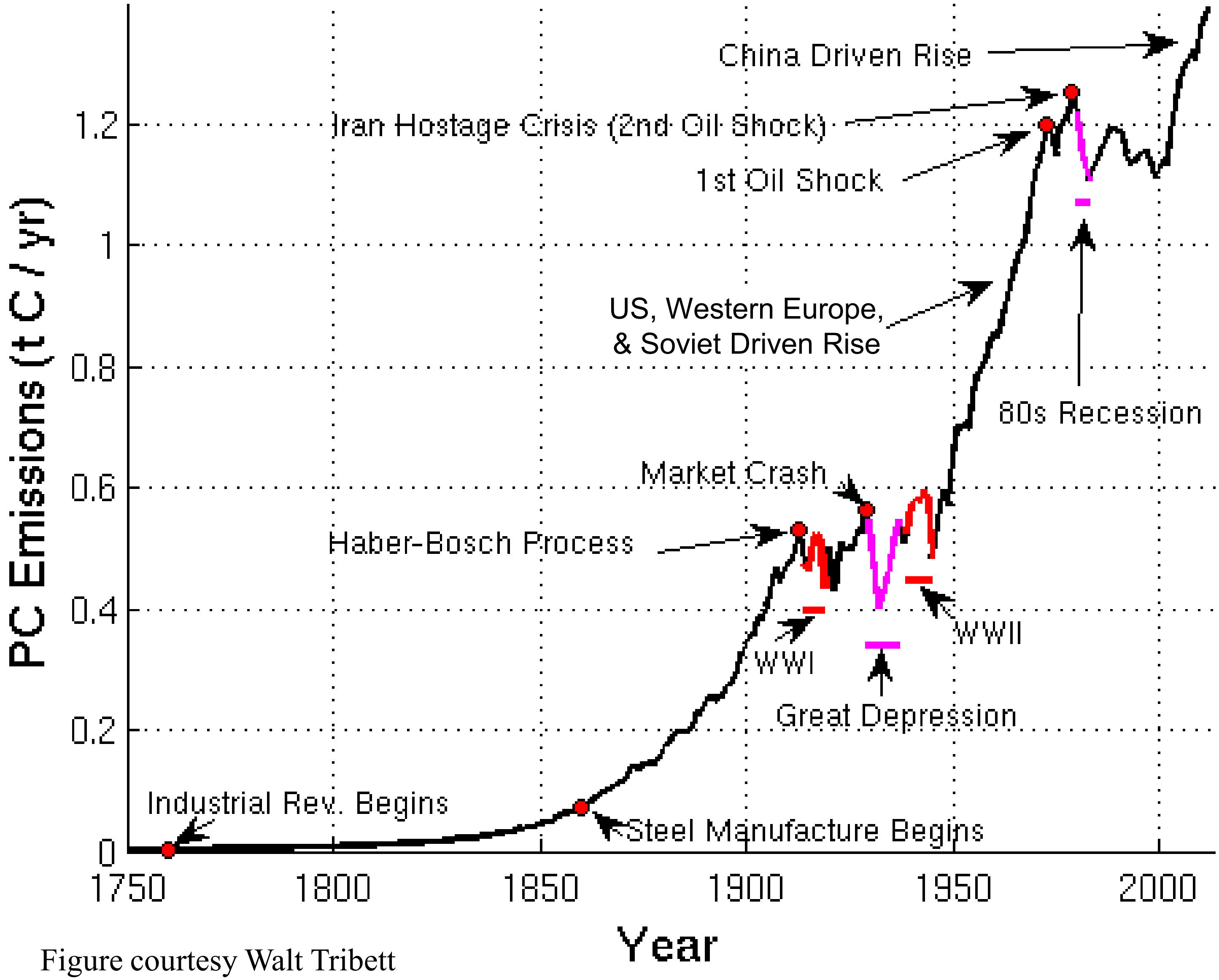
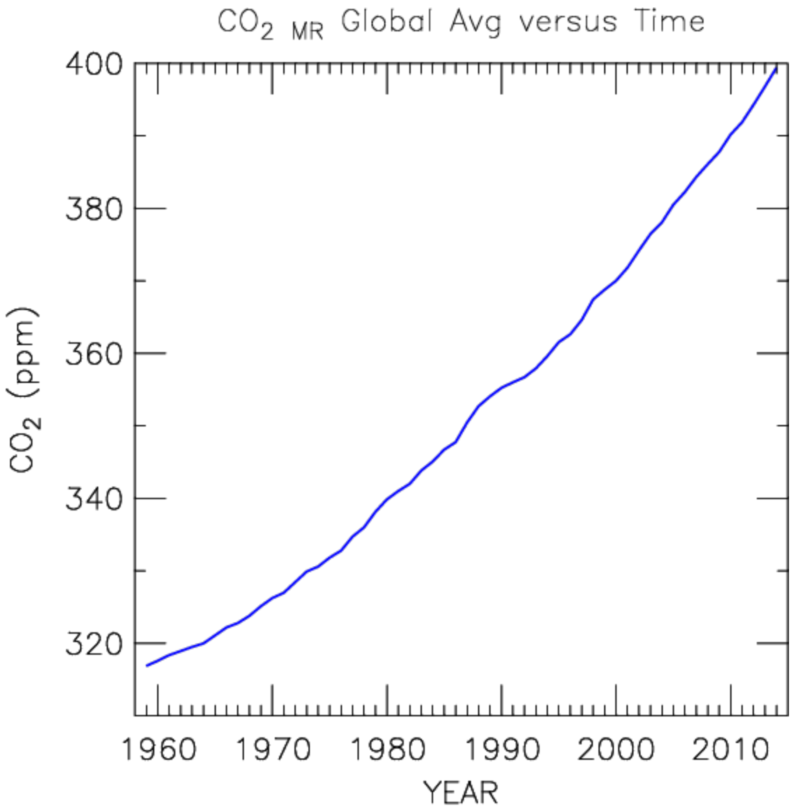
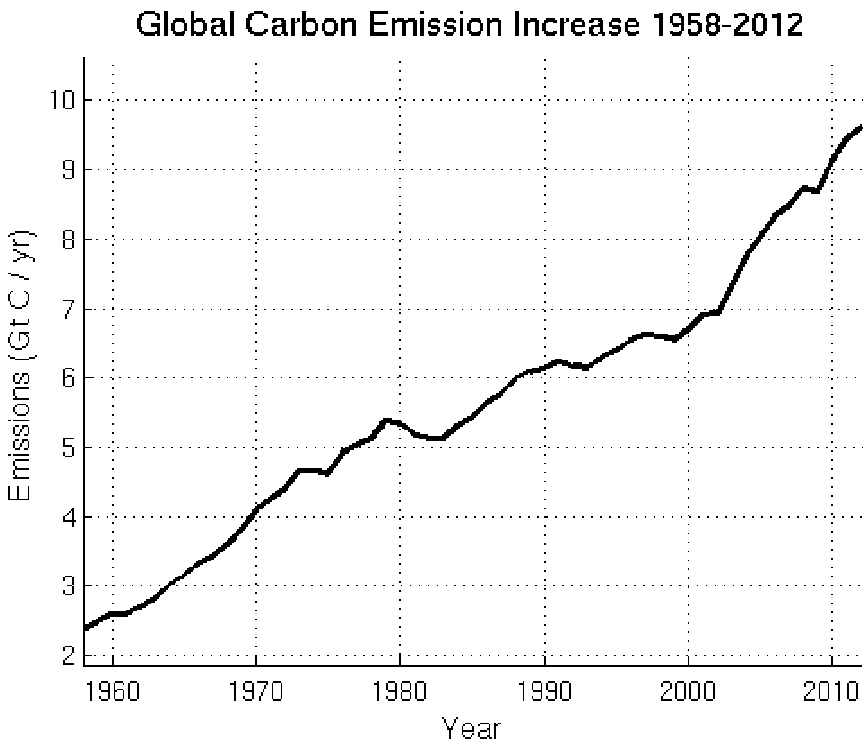


Figure courtesy Walt Tribett


$CO_{2\ MR}$ Global Avg versus Time


Global Carbon Emission Increase 1958-2012

Δ mass of atmospheric C, 1959 to 2012 = **Gt C**

Fossil Fuel Emissions, 1959 to 2012 = **305 Gt C**

Atmospheric CO_2 since ~1860

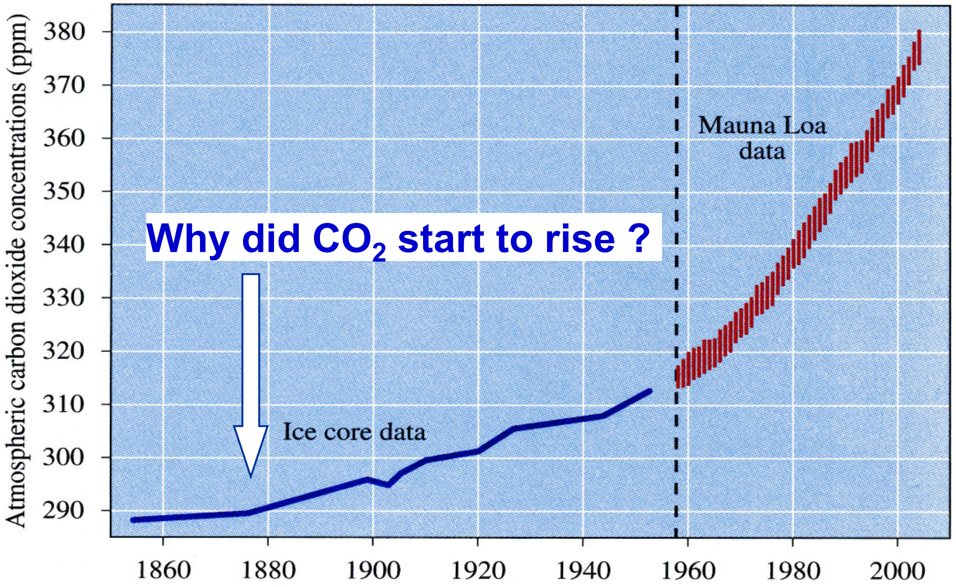


Figure 3.5, *Chemistry in Context*
6th Edition

Global Carbon Cycle

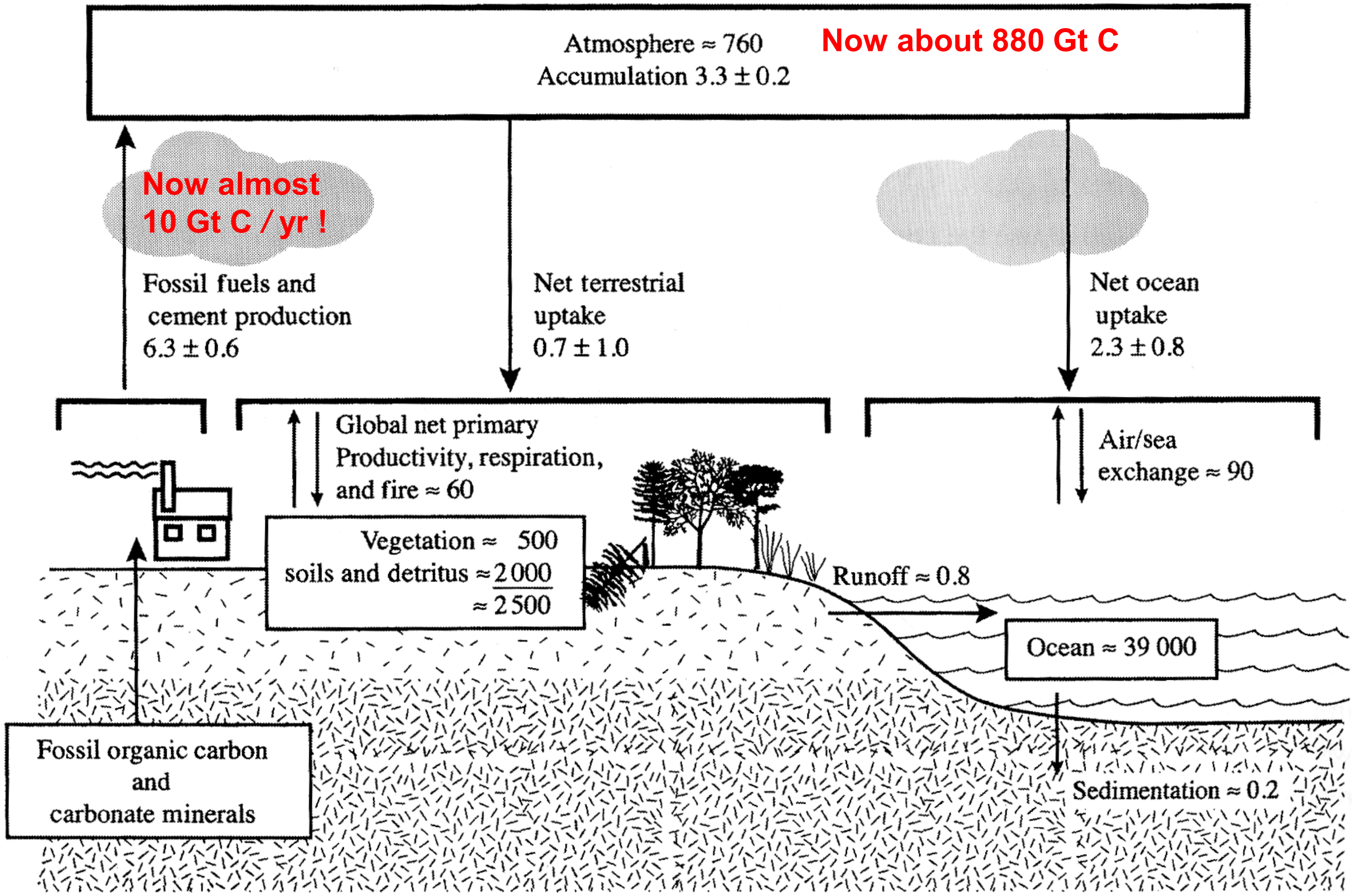
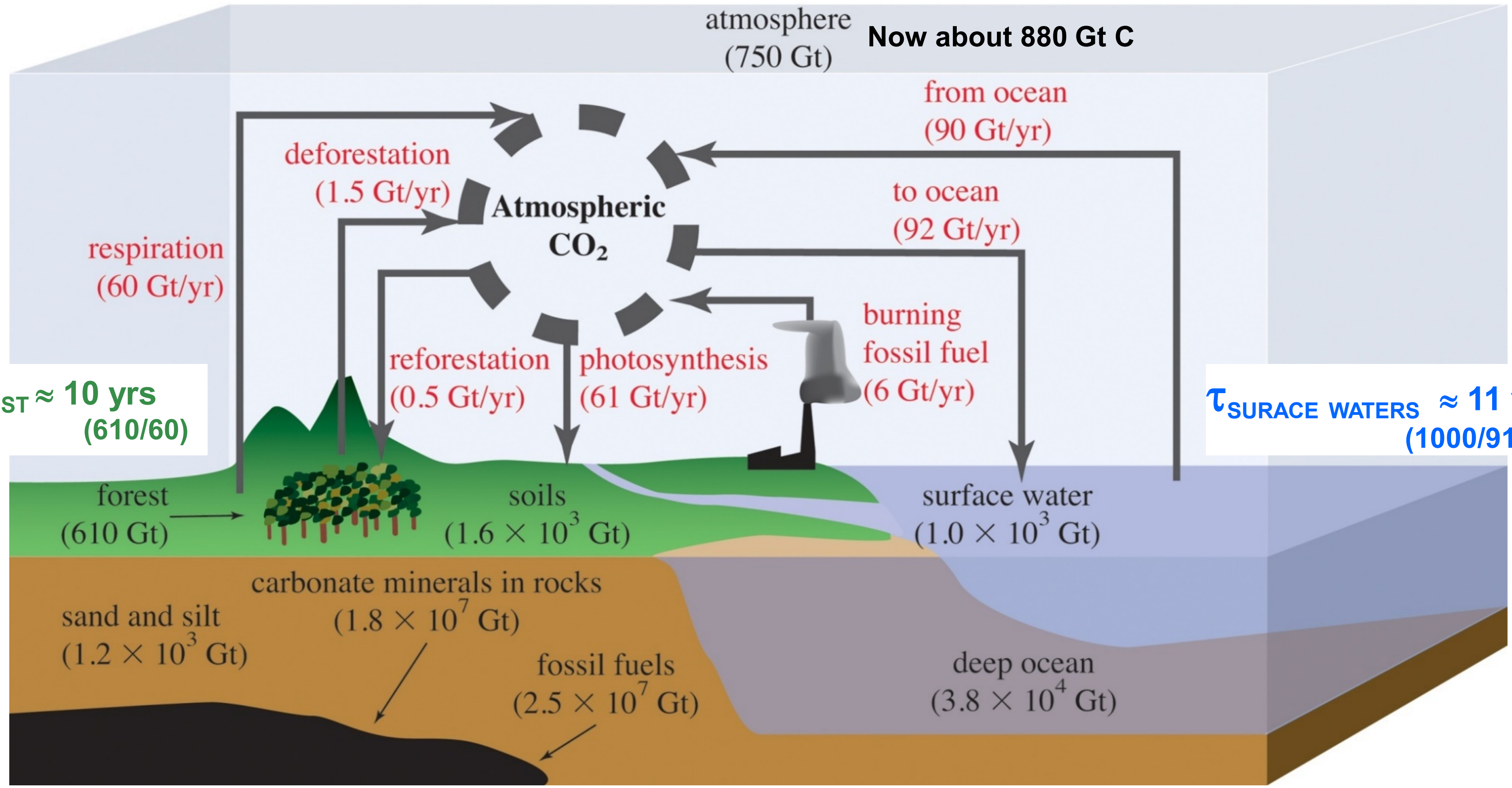


Figure 3.1 The global carbon cycle, showing the carbon stocks in reservoirs (in Gt) and carbon flows (in Gt year^{-1}) relevant to the anthropogenic perturbation as annual averages over the decade from 1989 to 1998. Net ocean uptake of the anthropogenic perturbation equals the net air/sea input plus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

Page 30, Houghton

Global Carbon Cycle



$\tau_{\text{FOREST}} \approx$ 10 yrs
(610/60)

$\tau_{\text{SURACE WATERS}} \approx$ 11 yrs
(1000/91)

$\tau_{\text{SEDIMENT}} \approx 1.6 \times 10^5$ yrs (RJS estimate)

$\tau_{\text{OCEAN}} \approx$ 430 yrs
(39000/91)

Fig 3.2, Chemistry in Context

CO_2 Is Long Lived

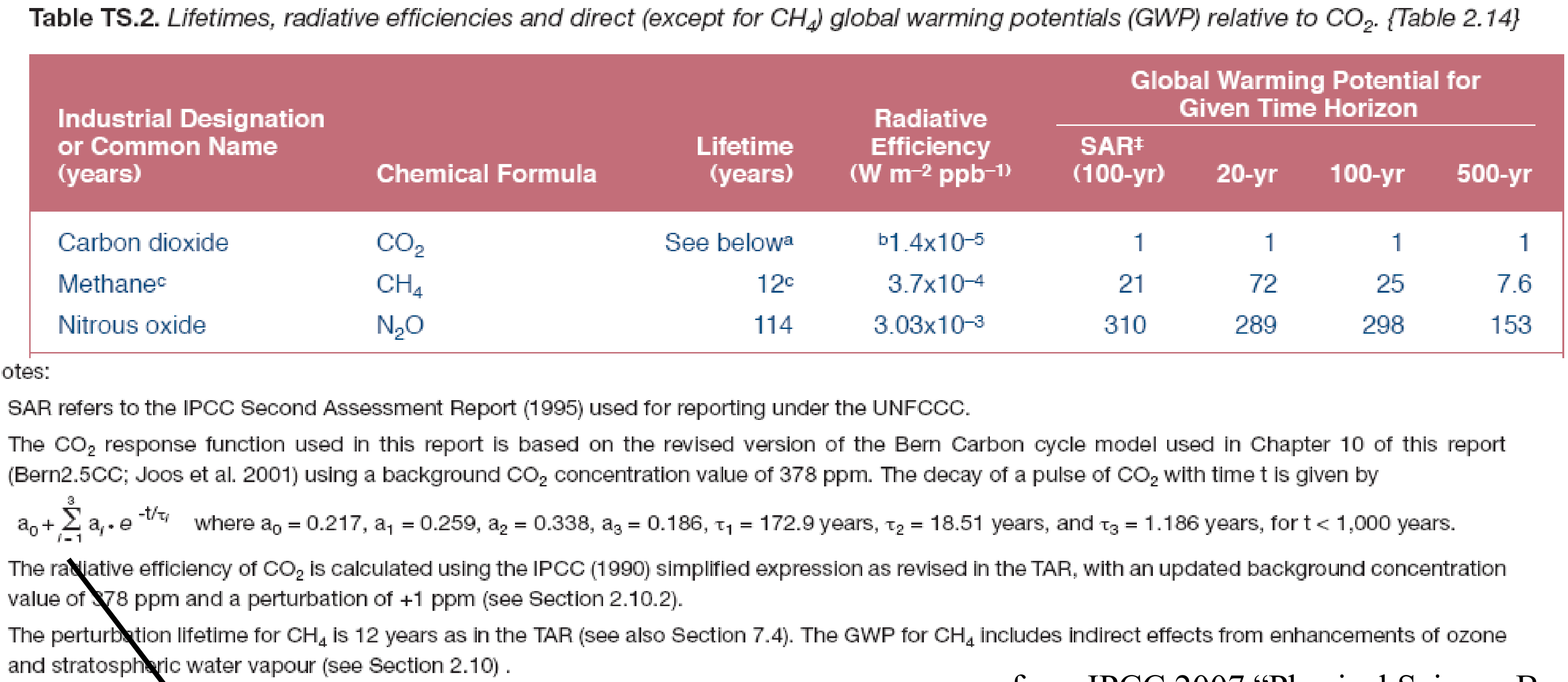


Table TS.2. *Lifetimes, radiative efficiencies and direct (except for CH_4) global warming potentials (GWP) relative to CO_2. {Table 2.14}*

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) .

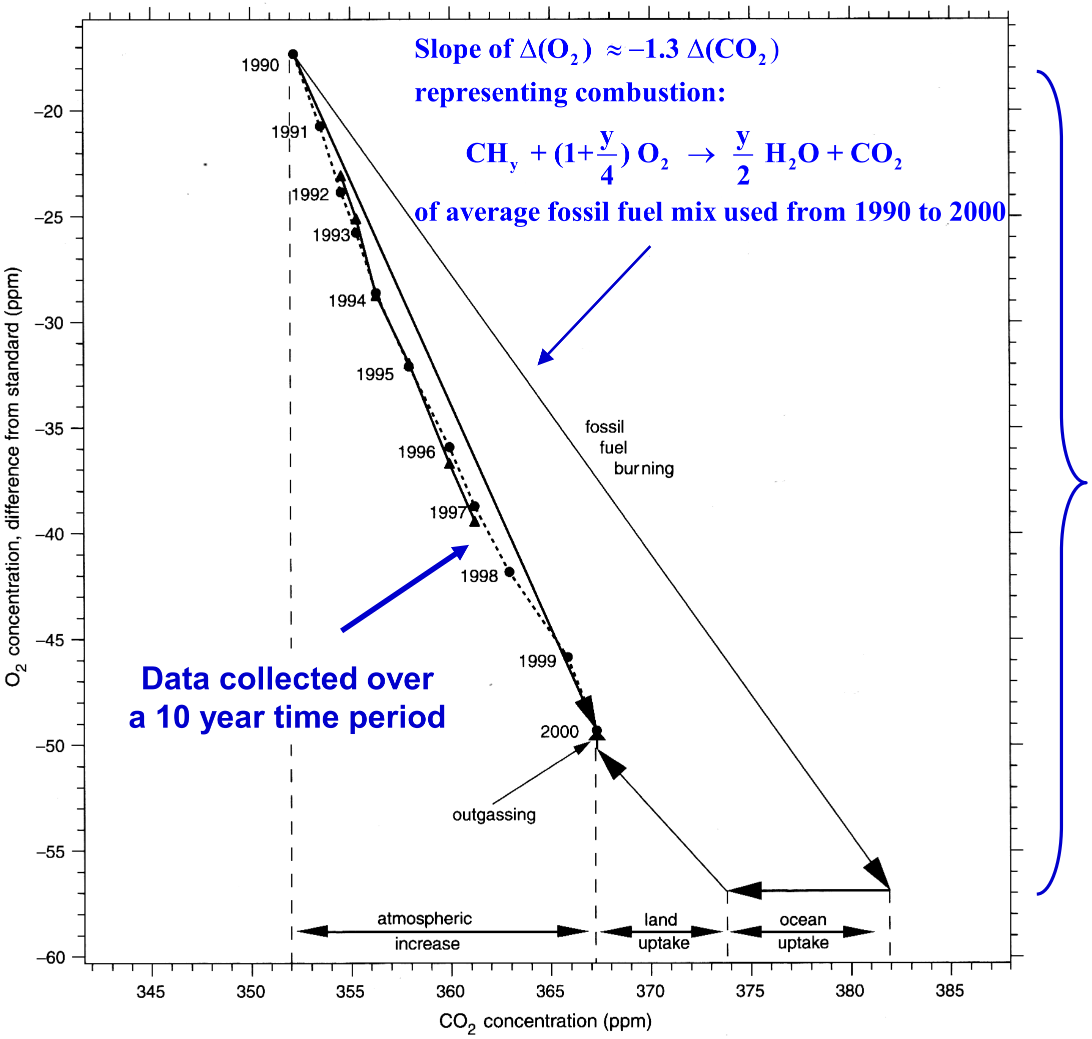
from IPCC 2007 “Physical Science Basis”

CO_2 has multiple time constants

Longest decay of IPCC formula is close to 200 years, which represents time for surface waters to equilibrate with the intermediate ocean

Note: IPCC formula should only be used for t <1000 years

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



Slope of $\Delta(O_2) \approx -1.3\ \Delta(CO_2)$ representing combustion:

$$CH_y + (1+\frac{y}{4})\, O_2 \rightarrow \frac{y}{2}\, H_2O + CO_2$$

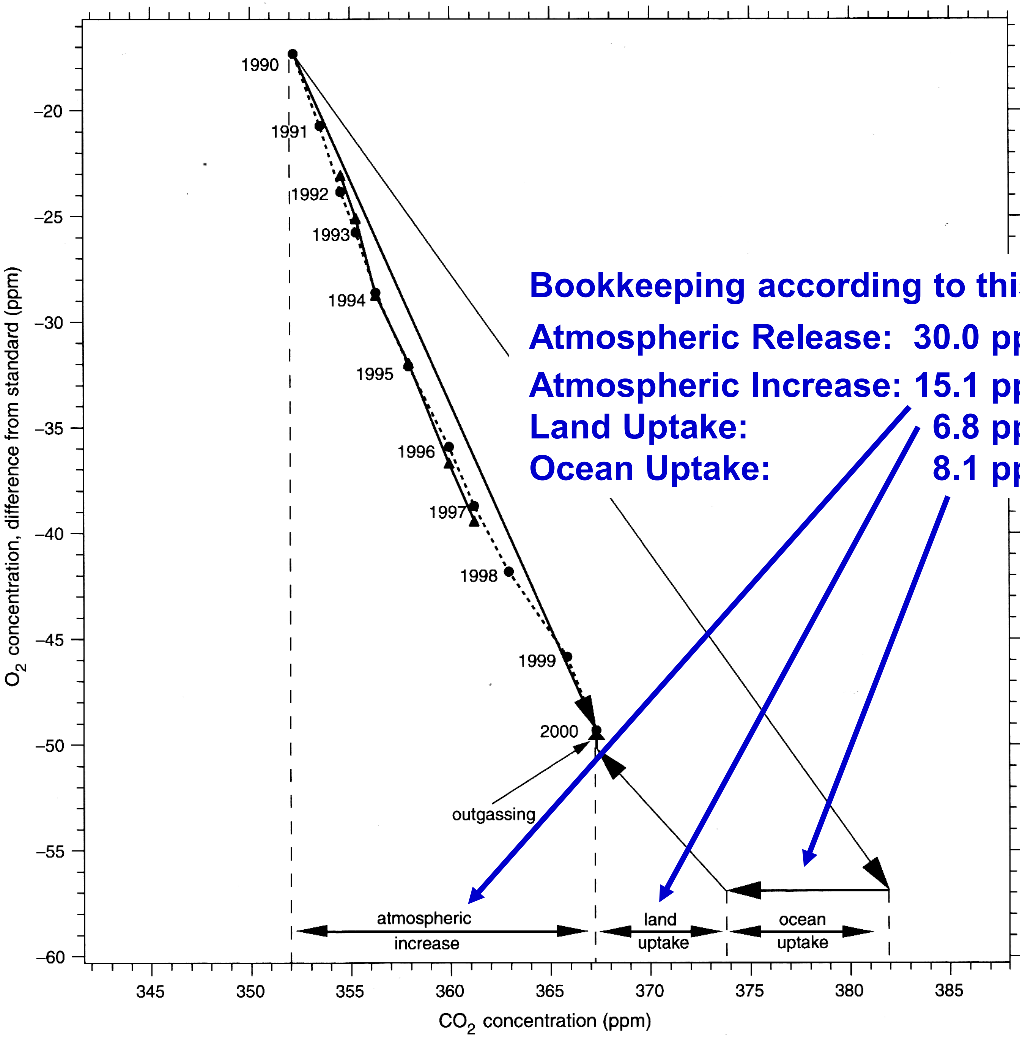
of average fossil fuel mix used from 1990 to 2000

Data collected over a 10 year time period

O_2 falls a tiny bit as CO_2 rises

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.

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

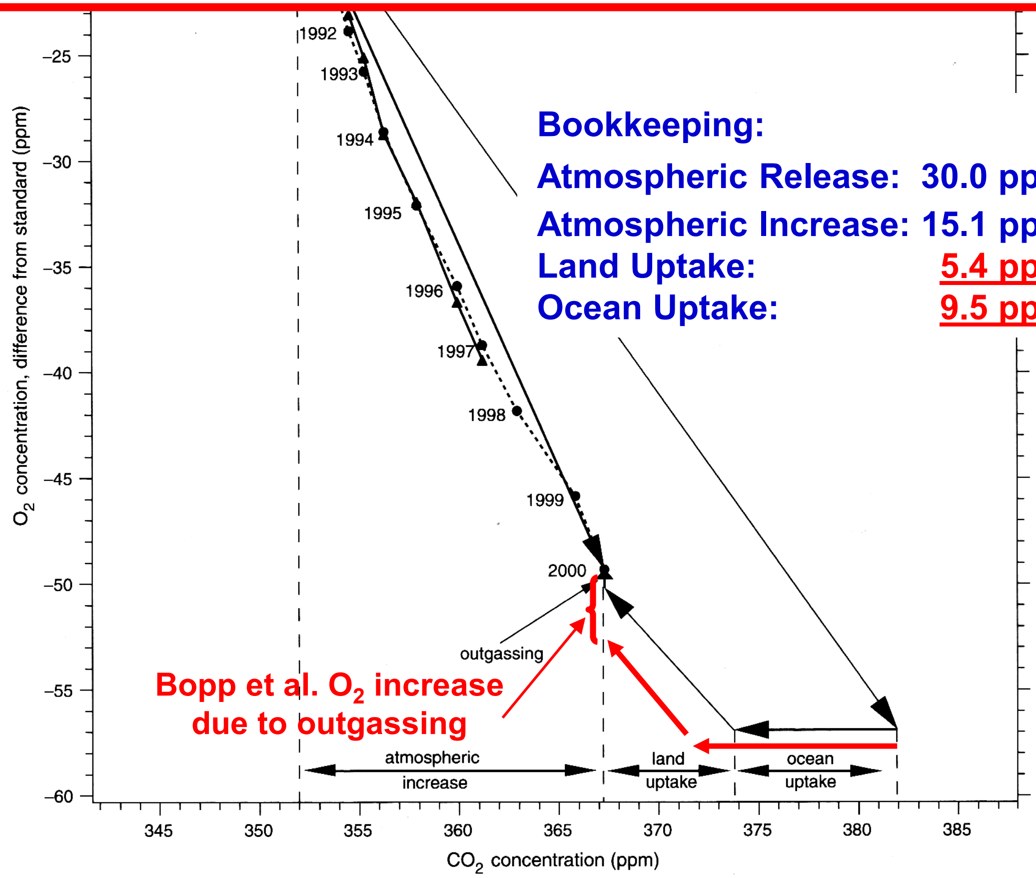


Bookkeeping according to this study:

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)**

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.

Note: As the ocean warms, O_2 solubility decreases.
In other words, as climate changes, the oceans outgas O_2.
Bopp et al. (GBC, 2002) applied a correction for
ocean outgassing and concluded:



Bopp et al. O_2 increase due to outgassing

Bookkeeping:

Atmospheric Release:	**30.0 ppm**	**(66 Gt)**
Atmospheric Increase:	**15.1 ppm**	**(~50% airborne fraction)**
Land Uptake:	**5.4 ppm**	**(36% of uptake)**
Ocean Uptake:	**9.5 ppm**	**(64% of uptake)**

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.

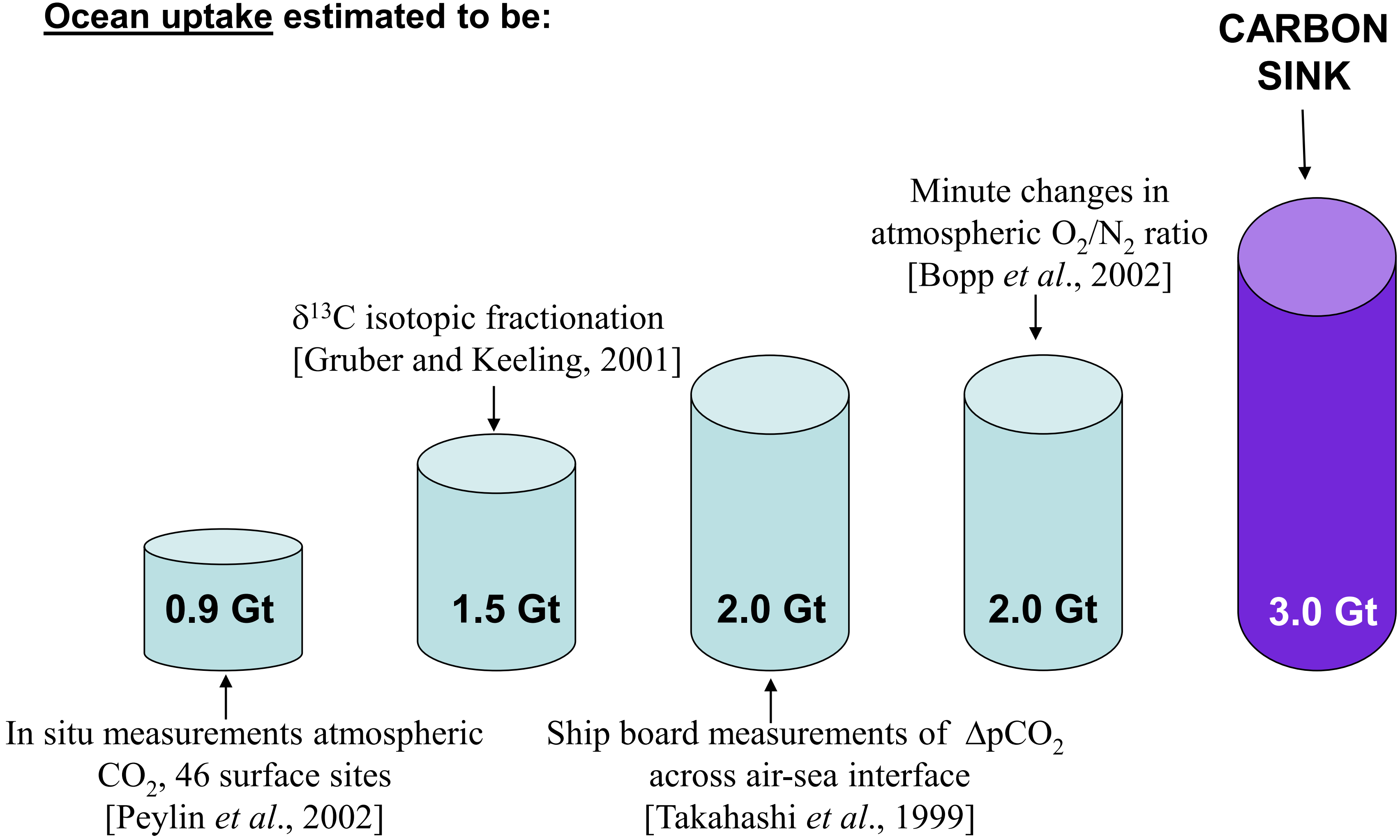
Global Carbon Cycle

Where is the CO_2 being sequestered?

During the 1990s, humans released ~6 Gt C/yr.

If ~50% stayed in atmosphere, then 0.5 × 6 Gt C/yr ≈ **3.0 Gt C/yr** went to land and oceans

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



CARBON SINK

Minute changes in atmospheric O_2/N_2 ratio [Bopp *et al*., 2002]

$\delta^{13}C$ isotopic fractionation [Gruber and Keeling, 2001]

In situ measurements atmospheric CO_2, 46 surface sites [Peylin *et al*., 2002]

Ship board measurements of ΔpCO_2 across air-sea interface [Takahashi *et al*., 1999]

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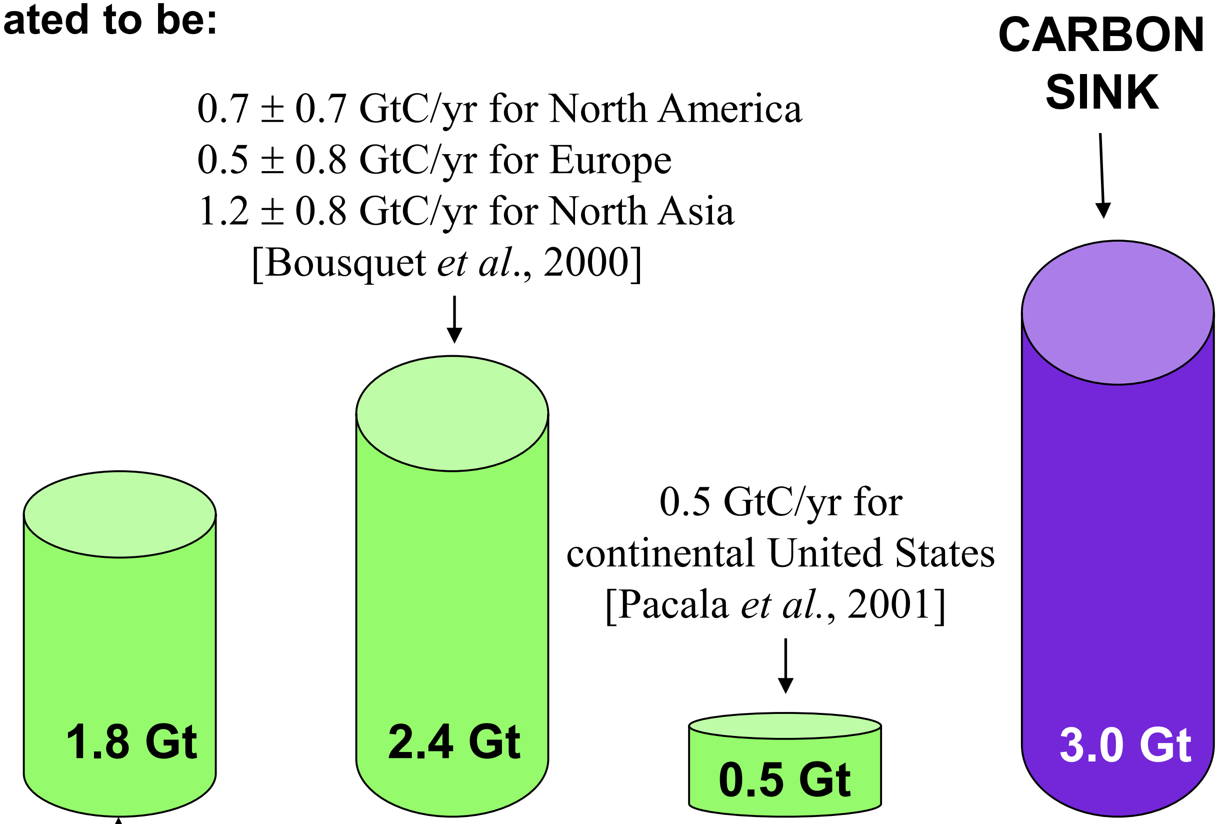


0.7 ± 0.7 GtC/yr for North America
0.5 ± 0.8 GtC/yr for Europe
1.2 ± 0.8 GtC/yr for North Asia
[Bousquet *et al*., 2000]

0.5 GtC/yr for
continental United States
[Pacala *et al*., 2001]

CARBON SINK

1.7 ± 0.5 GtC/yr for North America
0.1 ± 0.6 GtC/yr for Eurasia/North Africa
[Fan *et al*., 1992]

Uptake of Atmospheric CO_2 by Trees (Land Sink)

Land sink: relatively short lived reservoir

- In this model, future water stress due to climate change eventually limits plant growth
- Feedbacks between climate change & plants lead to almost 100 ppm additional CO_2 by end of century

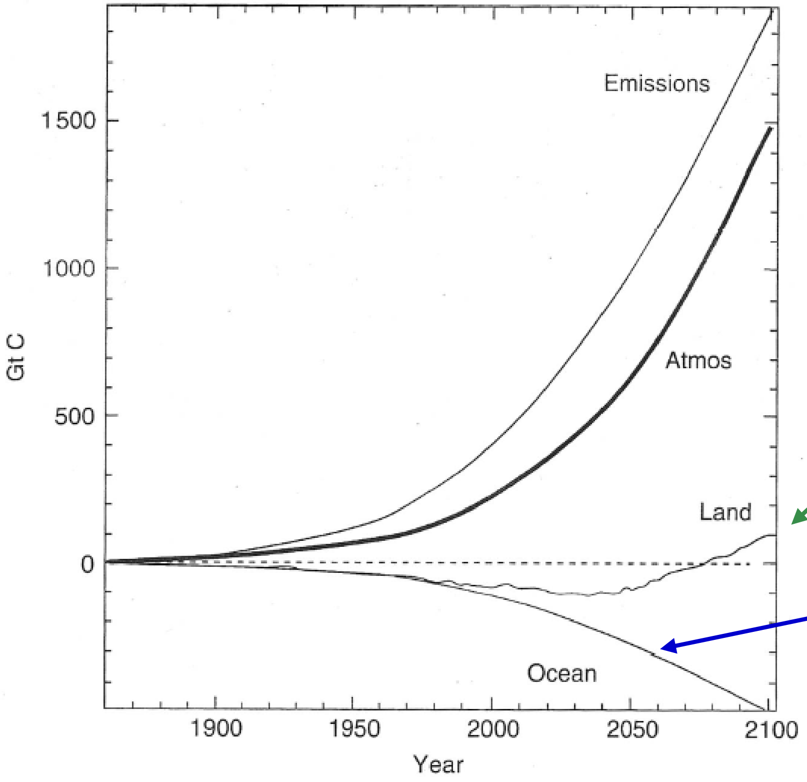


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

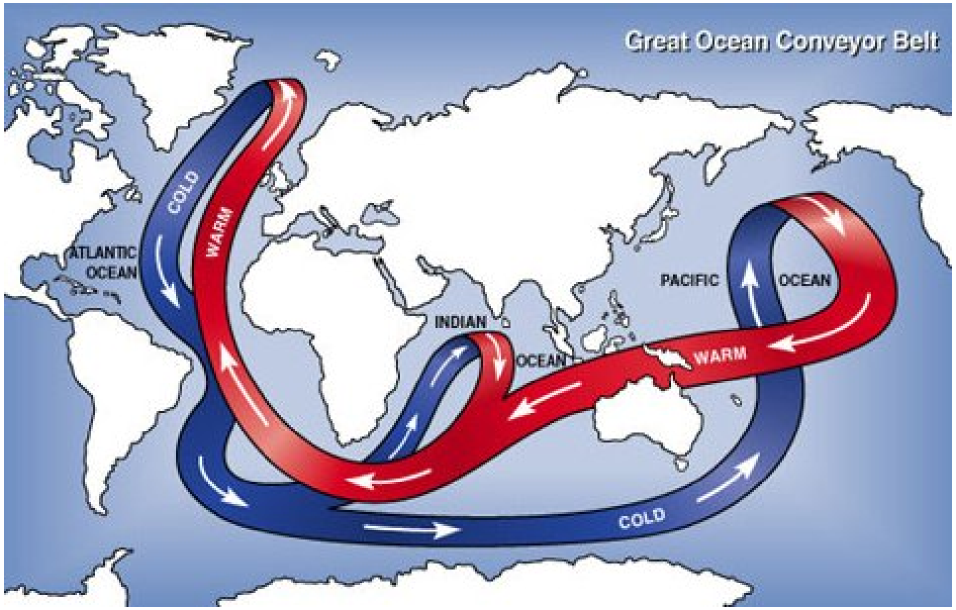
Page 41, Houghton

Ocean sink: relatively long lived reservoir

In nearly all models, ocean uptake slows relative to rise in atmospheric CO_2

Uptake of Atmospheric CO_2 by Oceans

- 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
  - b) Deep water forms at high latitude. As deep water sinks, ocean carbon (ΣCO_2) accumulated at the surface is moved to the deep ocean interior.
- Biological Pump:
  - a) Ocean biology limited by availability of nutrients such as NO_3^-, PO_4^-, and Fe^{2+} & Fe^{3+} . Ocean biology is never carbon limited.
  - 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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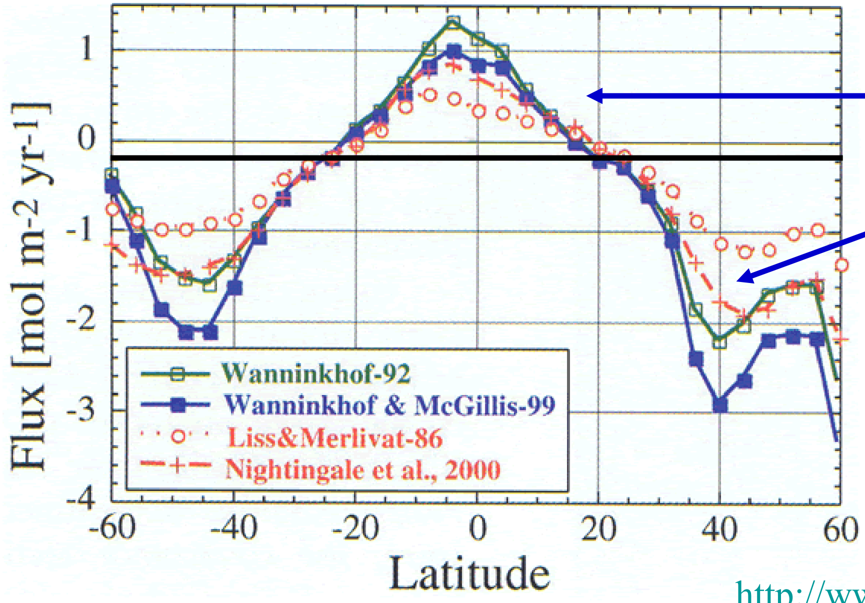

CO_2 comes out of tropical ocean

CO_2 goes into rest of the ocean

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

Uptake of Atmospheric CO_2 by Oceans

When CO_2 dissolves:

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

Atmospheric CO_2	280 ppm Pre-Industrial	400 ppm Present Day	560 ppm 2 × Pre-Indus.
Ocean Carbon	2020×10^{-6} M	2075×10^{-6} M	2122×10^{-6} M
$[HCO_3^-]$	1772×10^{-6} M	1875×10^{-6} M	1957×10^{-6} M
$[CO_2\,(aq)]$	9.1×10^{-6} M	13.0×10^{-6} M	18.2×10^{-6} M
$[CO_3^{2-}]$	239×10^{-6} M	188×10^{-6} M	146×10^{-6} M
pH	8.32	8.19	8.06

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

Notes:

$T = 293$ K; Alkalinity= 2.25×10^{-3} M

M ≡ mol/liter

Mathematics supporting this calculation on Extra Slide 3

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$[CO_3^{2-}]$	239×10^{-6} M	188×10^{-6} M	146×10^{-6} M
pH	8.32	8.19	8.06

$$\text{Revelle Factor} = \frac{\Delta\text{Ocean Carbon} / \langle \text{Ocean Carbon} \rangle_{\text{AVERAGE}}}{\Delta\text{Atmos}_{\text{CO2}} / \langle \text{Atmos}_{\text{CO2}} \rangle_{\text{AVERAGE}}}$$

$$= \frac{55/2047.5}{120/340} = 0.076 \text{ (from pre-industrial to present-day } CO_2\text{)}$$

$$= \frac{47/2098.5}{160/480} = 0.067 \text{ (from present-day to } 2\times \text{ pre-industrial } CO_2\text{)}$$

Biology in Today's Ocean

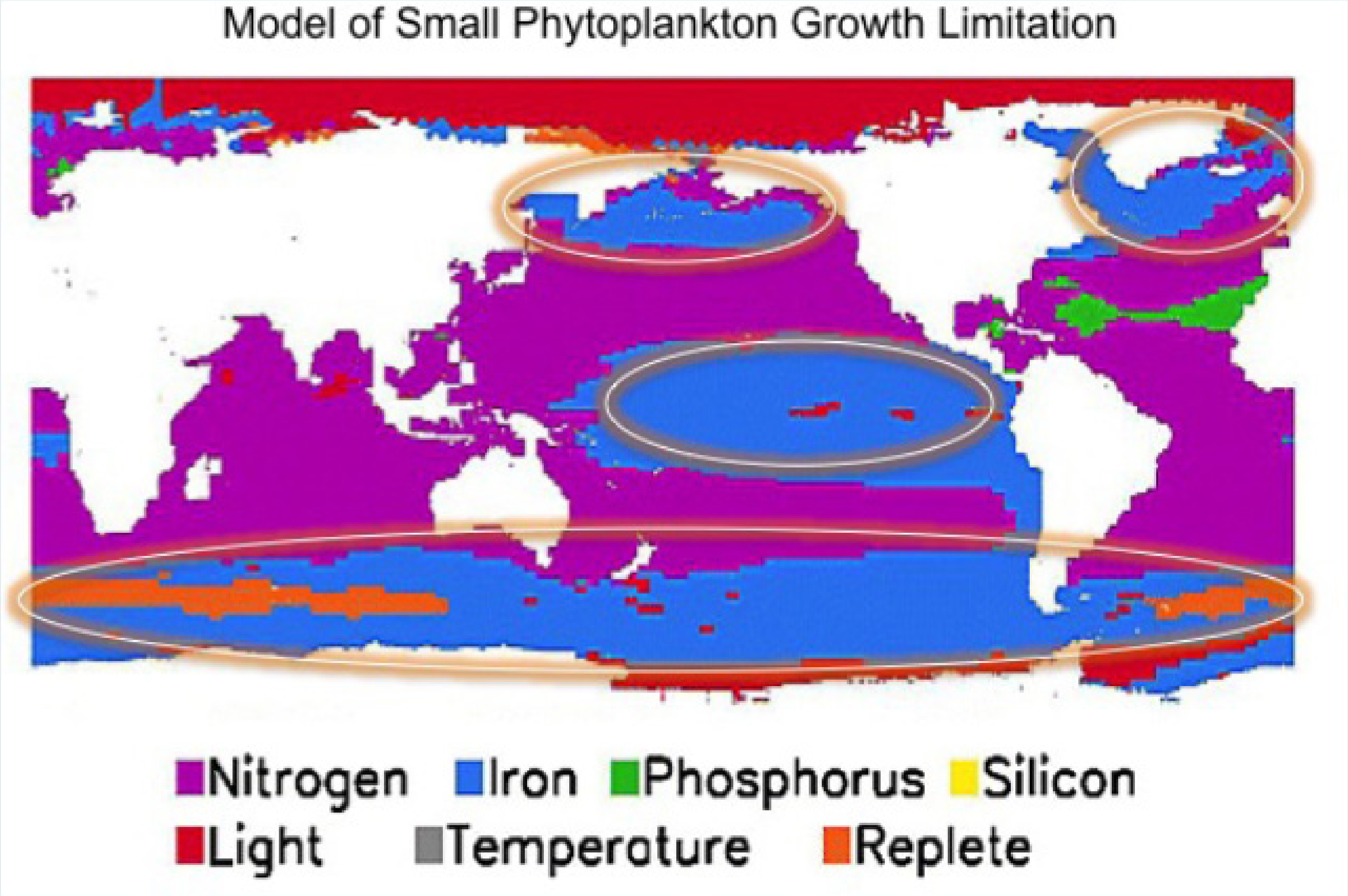
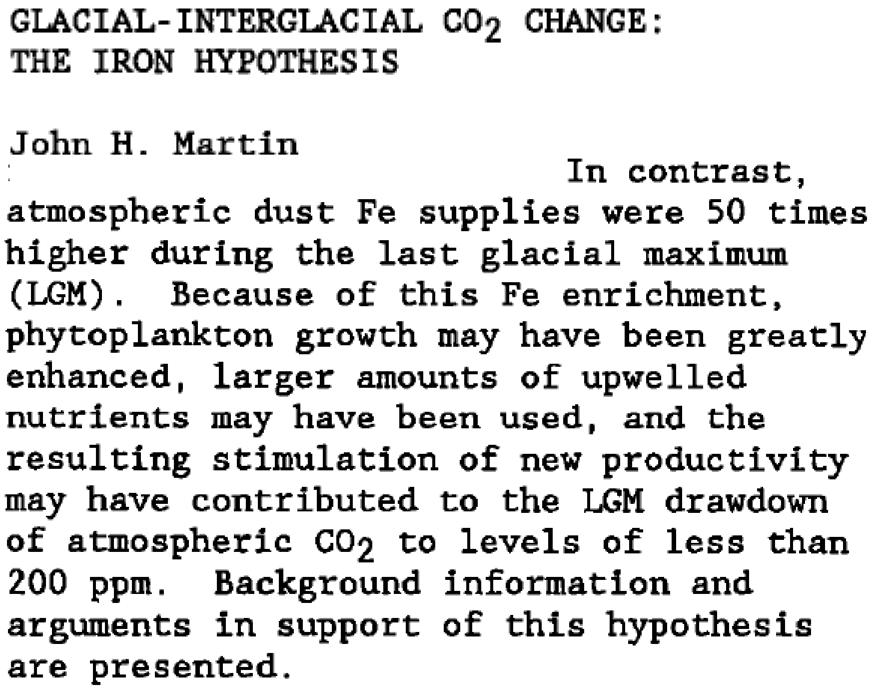


Figure 1. Results of a global model of small phytoplankton growth limitation by Moore et al. 2004 (*Global Biogeochemical Cycles*). Blue shaded areas denote regions that are potentially limited by iron availability. Iron is supplied by dust from continents and by upwelling of deep water. However, high iron demand in the euphotic zone quickly drives iron concentrations to nano- and picomolar levels that can be limiting to many phyto- and bacterioplankton.

http://www.whoi.edu/page.do?pid=130796

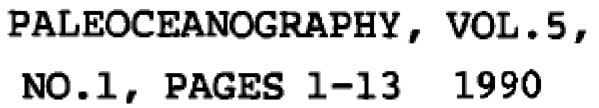
Connection to Glacial CO_2



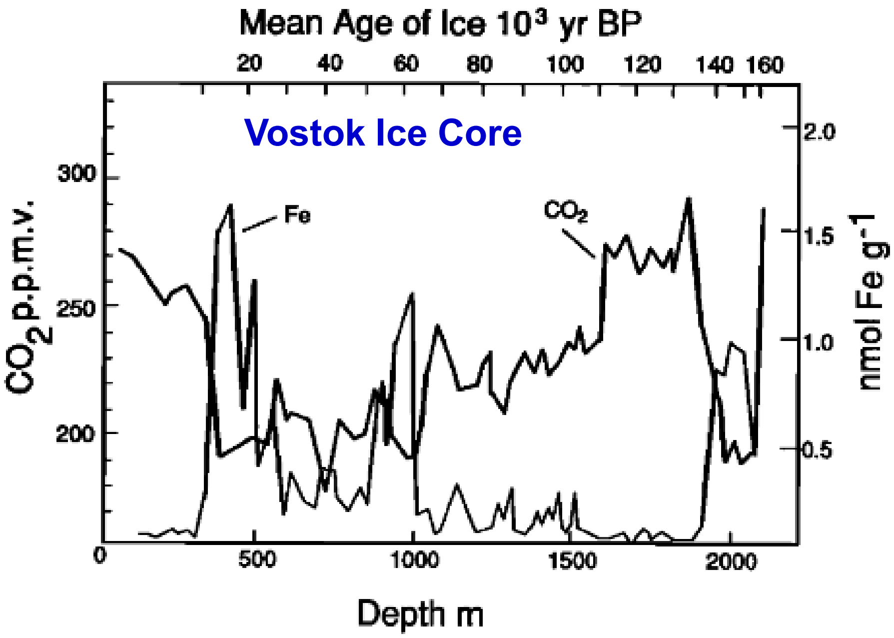
GLACIAL-INTERGLACIAL CO_2 CHANGE:
THE IRON HYPOTHESIS

John H. Martin

In contrast, atmospheric dust Fe supplies were 50 times higher during the last glacial maximum (LGM). Because of this Fe enrichment, phytoplankton growth may have been greatly enhanced, larger amounts of upwelled nutrients may have been used, and the resulting stimulation of new productivity may have contributed to the LGM drawdown of atmospheric CO_2 to levels of less than 200 ppm. Background information and arguments in support of this hypothesis are presented.



PALEOCEANOGRAPHY, VOL.5,
NO.1, PAGES 1-13 1990

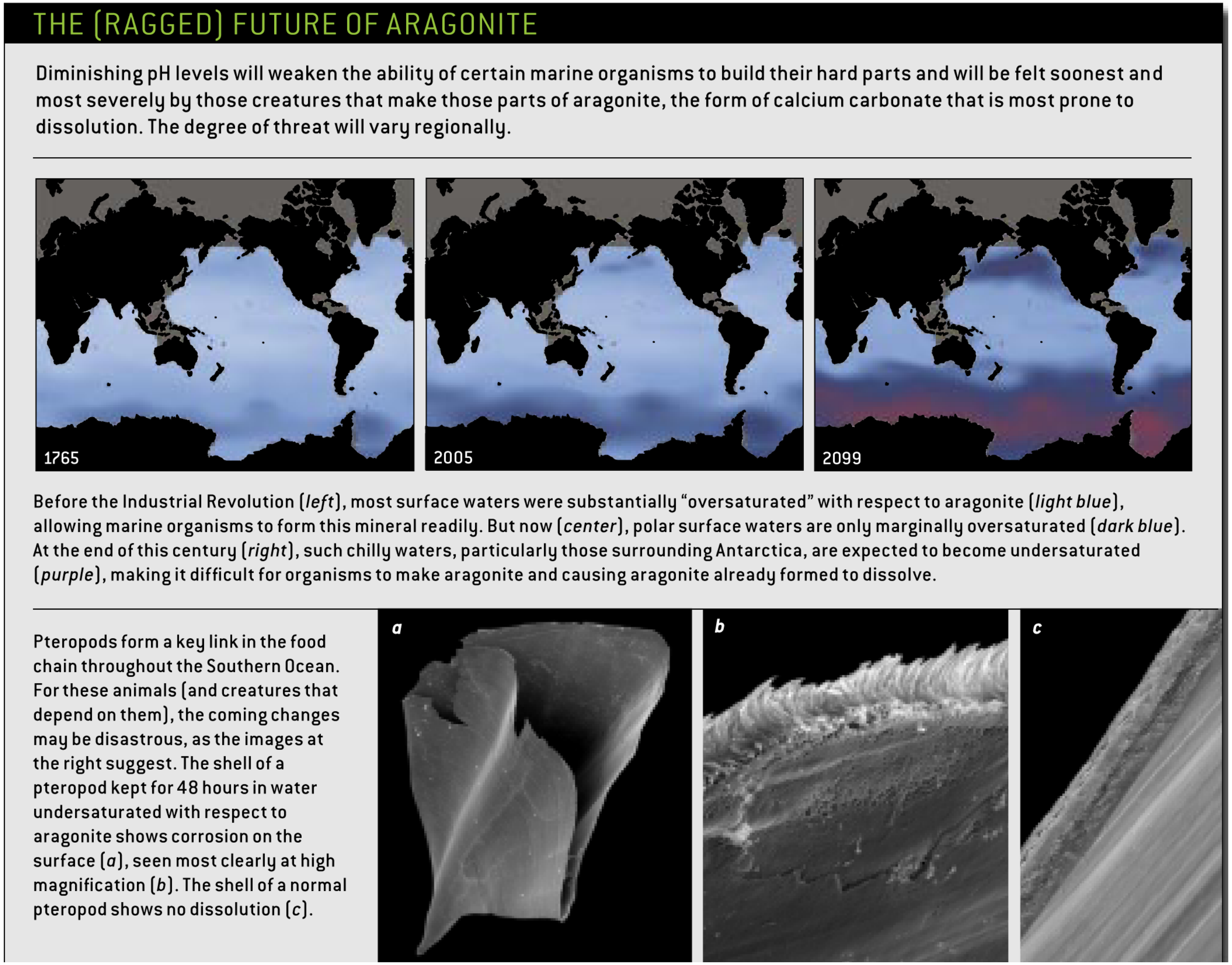


See http://onlinelibrary.wiley.com/doi/10.1029/PA005i001p00001/abstract

Uptake of Atmospheric CO_2 by Oceans

Future ocean uptake of atmospheric CO_2 will lead 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

Uptake of Atmospheric CO_2 by Trees (Land Sink)

Land sink: relatively short lived reservoir

- In this model, future water stress due to climate change eventually limits plant growth
- Feedbacks between climate change & plants lead to almost 100 ppm additional CO_2 by end of century

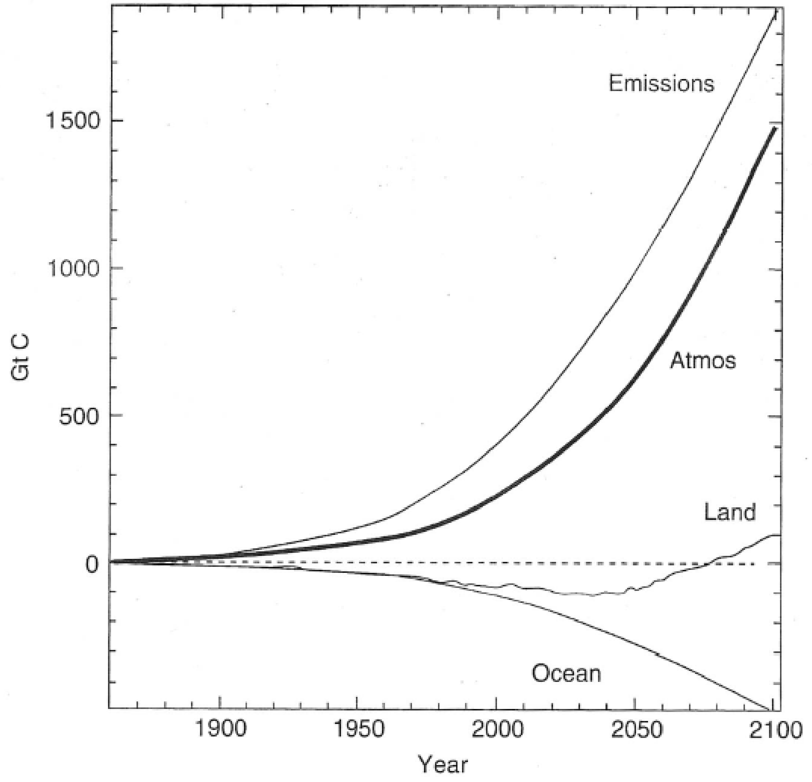


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbo cycle. Results are shown of the changing budgets of carbon

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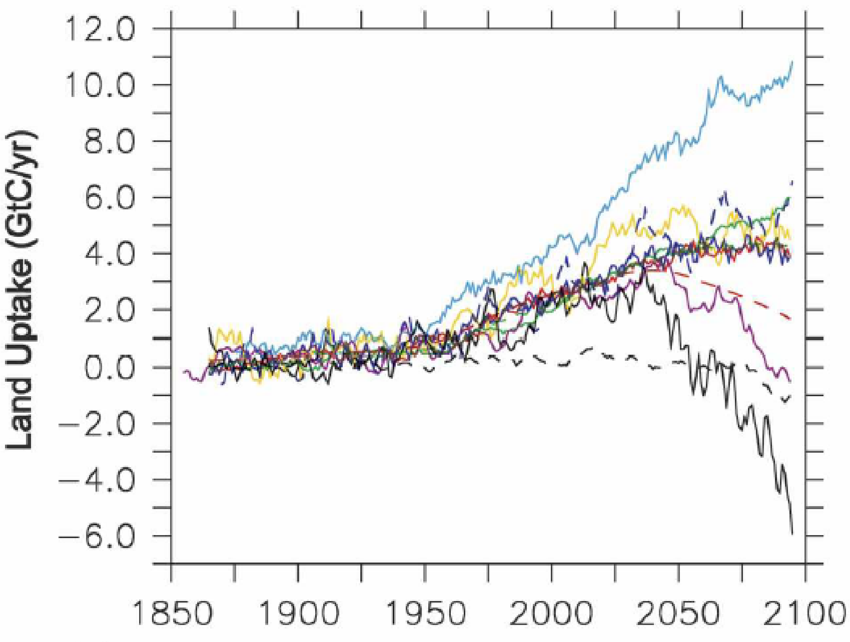
- Future fate of land sink highly uncertain according to **11** coupled climate-carbon cycle models examined by Friedlingstein et al. (2006)



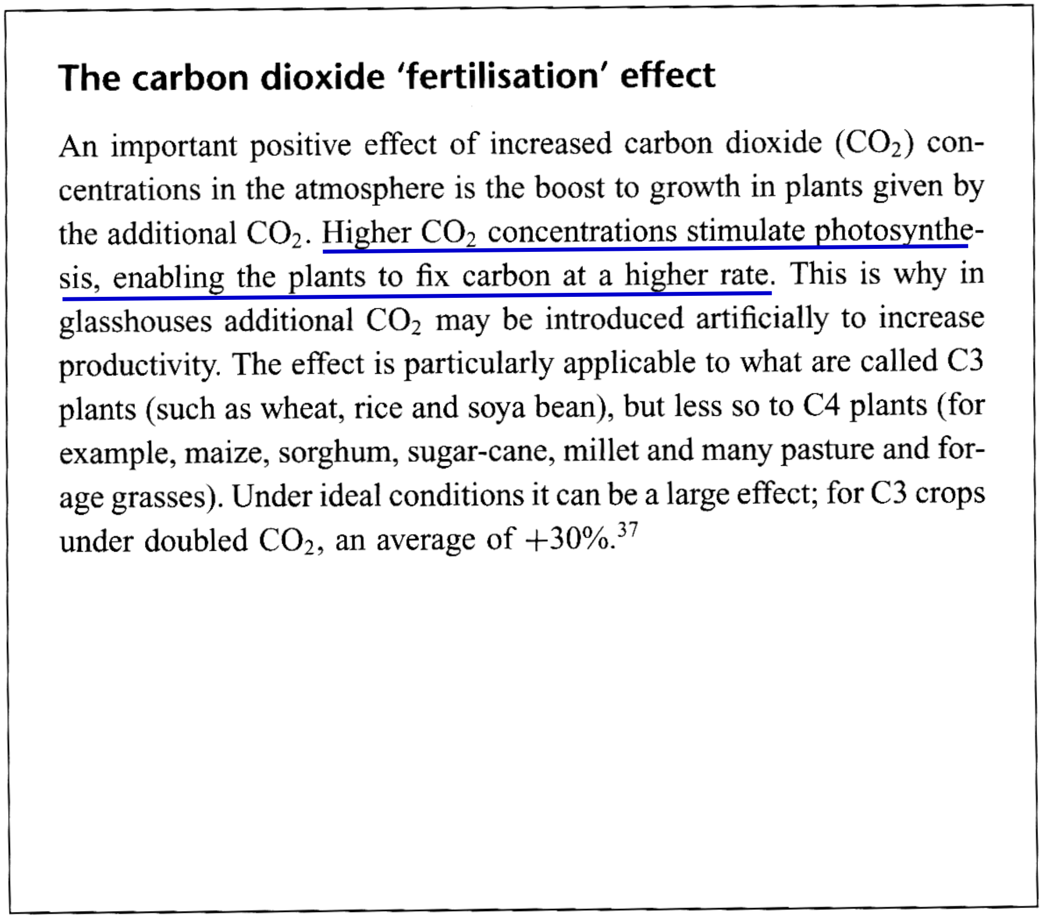
Uptake of Atmospheric CO_2 by Trees (Land Sink)

Land sink

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

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

Difficult to quantify because:



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]

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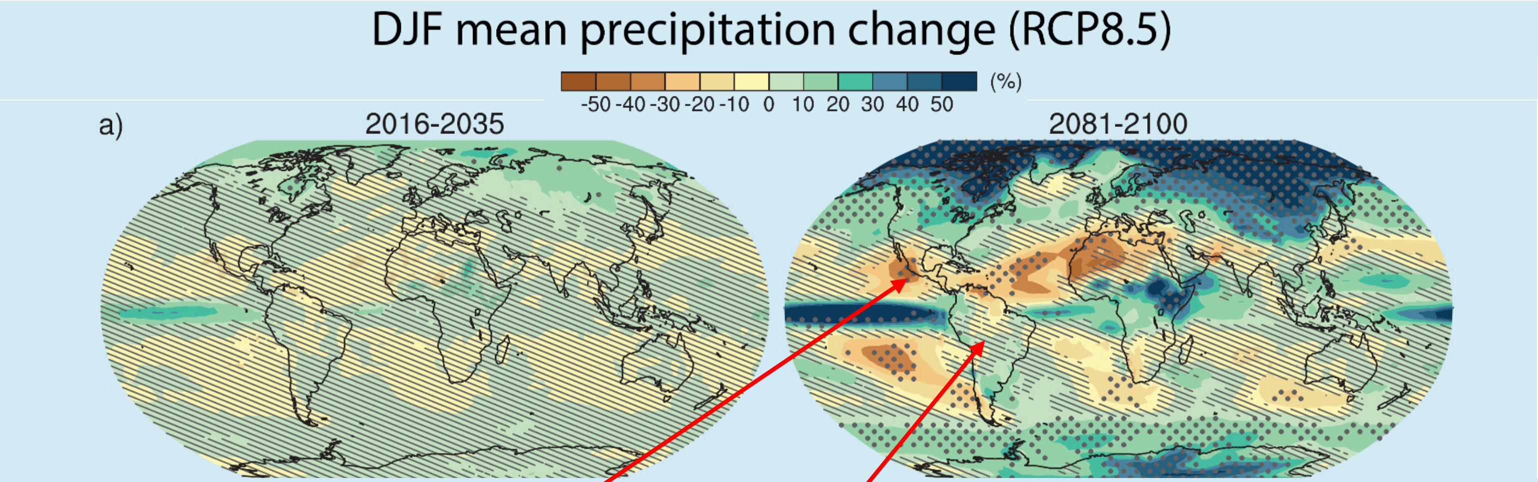
Uptake of Atmospheric CO_2 by Trees (Land Sink)

One more problem: Friedlingstein (2006) changes in land uptake are driven by future drought, and future precipitation is notoriously difficult to predict



Method (a): The default method used in Chapters 11,12 and 14 as well as in the Annex I (hatching only) is shown in Box 12.1, Figure 1a, and is based on relating the climate change signal to internal variability in 20-year means of the models as a reference[3]. Regions where the multi-model mean change exceeds two standard deviations of internal variability and where at least 90% of the models agree on the sign of change are stippled and interpreted as 'large change with high model agreement'. Regions where the model mean is less than one standard deviation of internal variability are hatched and interpreted as 'small signal or low agreement of models'. This can have various reasons: (1) changes in individual models are smaller than internal variability, or (2) although changes in individual models are significant, they disagree about the sign and the multi-model mean change remains small. Using this method, the case where all models scatter widely around zero and the case where all models agree on near zero change therefore are both hatched (e.g., precipitation change over the Amazon region by the end of the 21st century, which the following methods mark as 'inconsistent model response').

Figure 1, Chapter 12, IPCC (2013)

Extra Slide 1

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 ?

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

For CO_2 = 390 ppm:

$$[CO_2(aq)] = 3.4 \times 10^{-2}\ M / atm\ 3.9 \times 10^{-4}\ atm = 1.326 \times 10^{-5}\ M$$

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

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

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

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

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

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

Can solve if we assume charge balance: $[H^+] = [HCO_3^-] + 2\,[CO_3^{2-}]$

- or – by taking a short-cut (see next slide)

Extra Slide 2

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 $p_{CO2} = 1.326 \times 10^{-5}$ M for present atmosphere

$[H^+]\,[HCO_3^-] = K_1\,[CO_2(aq)] = 4.3 \times 10^{-7}\ \mathrm{M} \times 1.326 \times 10^{-5}\ \mathrm{M} = 5.70 \times 10^{-12}\ \mathrm{M}^2$

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

i.e., that $[H^+] \approx [HCO_3^-]$ and that both are >> $[CO_3^{2-}]$

$[H^+]\,[H^+] = 5.70 \times 10^{-12}\ \mathrm{M}^2 \Rightarrow\ [H^+] = 2.388 \times 10^{-6}$ M

pH $= -\log_{10}[H+] =$ ***5.6*** (390 ppm, 298 K)

Is the ***assumption*** justified? :

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

$[H^+]$ & $[HCO_3^-]$ are both ~ 2.4×10^{-6} M which is >> 4.7×10^{-11} M

Extra Slide 3

Ocean Acidity

As noted in class, the actual ocean is basic. The net charge from a series of **cations** (positively charged ions) and minor **anions** (negatively charged ions) is balanced by the total negative charge of the bicarbonate and carbonate ions. We write:

$$[\mathrm{Alk}] = [\mathrm{HCO_3^-}] + 2\,[\mathrm{CO_3^{2-}}] = [\mathrm{Na^+}]+[\mathrm{K^+}]+2[\mathrm{Mg^{2+}}]+2[\mathrm{Ca^{2+}}]-[\mathrm{Cl^-}]-[\mathrm{Br^-}]-2\,[\mathrm{SO_4^{2-}}] + \ldots$$

where Alk stands for Alkalinity

Henry's Law and the equations for the first and second dissociation constants yield:

$$\mathrm{pCO_2(vmr)} = \frac{[\mathrm{CO_2\ (aq)}]}{\alpha} \qquad \mathrm{K_1} = \frac{[\mathrm{HCO_3^-}]\,[\mathrm{H^+}]}{[\mathrm{CO_2(aq)}]} \qquad \mathrm{K_2} = \frac{[\mathrm{CO_3^{2-}}]\,[\mathrm{H^+}]}{[\mathrm{HCO_3^-}]}$$

The three equations above can be re-arranged to yield: $\mathrm{pCO_2(vmr)} = \left(\frac{\mathrm{K_2}}{\alpha \mathrm{K_1}}\right)\frac{[\mathrm{HCO_3^-}]^2}{[\mathrm{CO_3^{2-}}]}$

If we substitute $[\mathrm{HCO_3^-}] = \mathrm{Alk} - 2\,[\mathrm{CO_3^{2-}}]$ into the eqn above, we arrive at a quadratic eqn for $[\mathrm{CO_3^{2-}}]$ as a function of $\mathrm{pCO_2}$ and Alk. Note that α, $\mathrm{K_1}$, and $\mathrm{K_2}$ vary as a function of temperature (T) and ocean salinity (S) (http://en.wikipedia.org/wiki/Salinity)

If T, Alk, & S are specified, it is straightforward to solve for $[\mathrm{CO_3^{2-}}]$ from the quadratic eqn.

Values for $[\mathrm{CO_2(aq)}]$, $[\mathrm{HCO_3^-}]$, and [H+] are then found from Henry's law & the dissoc eqns.

Finally, Ocean Carbon is found from $[\mathrm{CO_2(aq)}]+[\mathrm{HCO_3^-}]+ [\mathrm{CO_3^{2-}}]$.