Global Carbon Cycle

AOSC / CHEM 433 & AOSC 633

Ross Salawitch & Walt Tribett

Class Web Sites:
http://www.atmos.umd.edu/~rjs/class/spr2019
https://myelms.umd.edu/courses/1256337
Email:
Ross: rsalawit@umd.edu or rjs@atmos.umd.edu; Walt: wtribett@umd.edu

Goals for today:

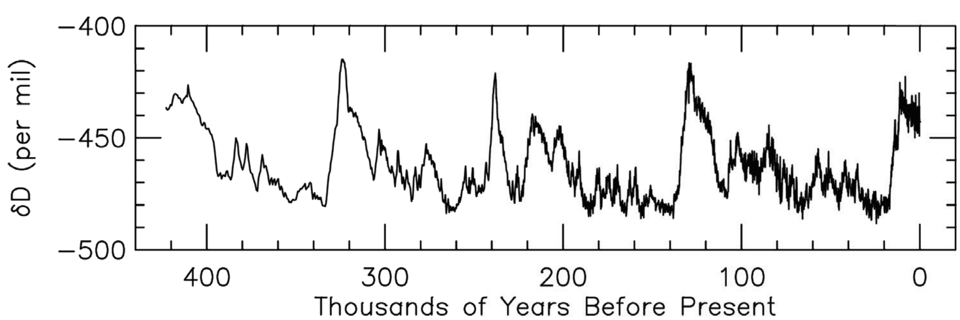
- **Overview of the Global Carbon Cycle "scratching below the surface"**
- **Ocean and land uptake of CO_2**
- **Connect to policy and long-term climate change**

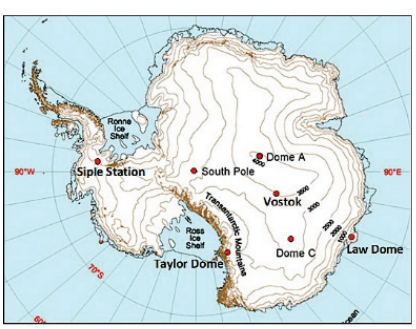
Lecture 5

14 February 2019

Vostok Ice Core

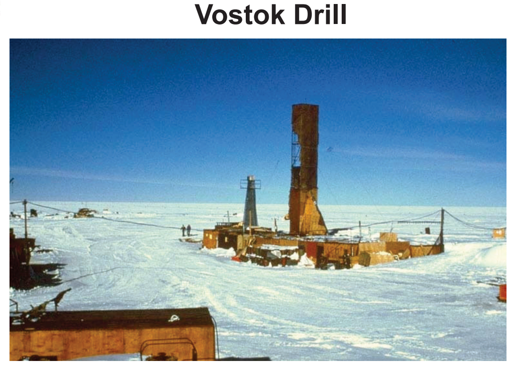
- January 1998: ice core with depth of 3.6 km extracted at Russian Vostok Station, Antarctica
- Vostok ice-core record extends back 400,000 years in time (Petit *et al.*, *Nature*, 1999)
- Reconstructed temperature based on measurement of the deuterium content of ice
- $\delta^{18}O$ shows tremendous variations in global ice volume (not shown)
- Ice core data show last four ice ages, punctuated by relatively brief interglacials





https://cdiac.ess-dive.lbl.gov/trends/co2/ice_core_co2.html

Vostok Drill



http://www.astrosurf.com/luxorion/Sciences/vostok-drill.jpg

Problem Set #1 has been modified

c) (10 points) Compute a new effective temperature for Earth, using the albedo found in part ii of Q1b.

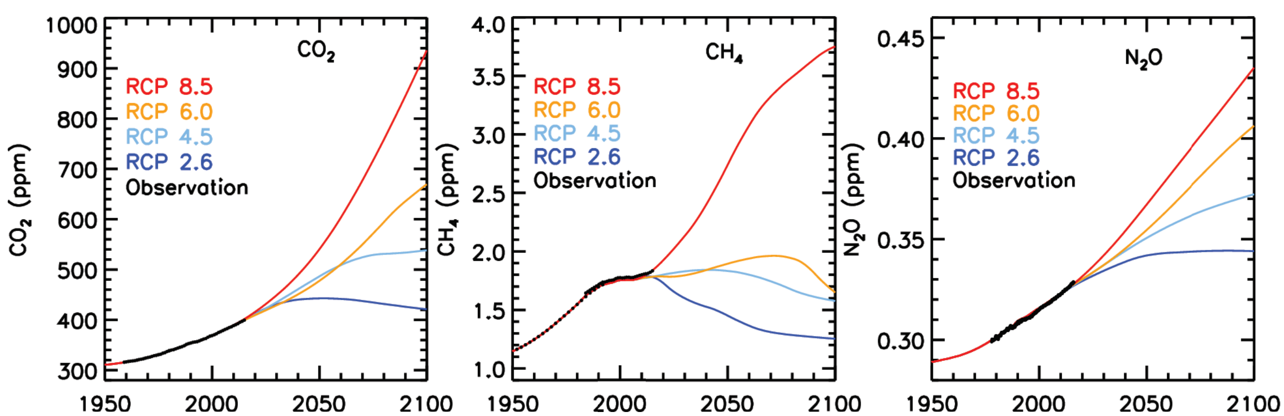
d) (10 points) Compare the two effective temperatures found in a) and c), and state whether:

i) the difference is physically consistent with the direction implied by the change in Earth's albedo that would result from a massive loss of sea-ice

ii) you think your calculations support the notion **that the "positive feedback": that is, a response (melting ice) to a driver (global warming) that re-inforces the initial action (warming) called the "ice-albedo" effect is a potentially important process.**

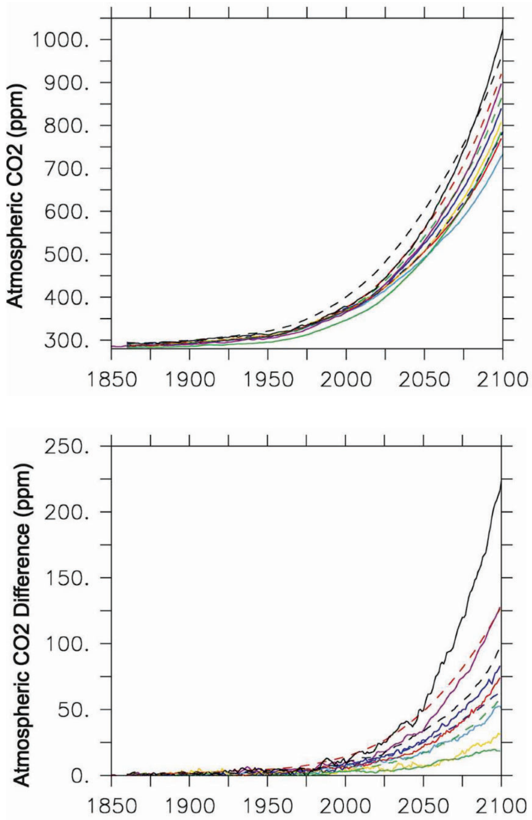
Note: there is also genuine concern about the impact of melting Arctic sea ice on the habitat for polar bears and the ecology of the Arctic. For ii) of this question, we would like your focus to be on the numerical calculations you have conducted.

Motivation 1



- RCP: Representative Concentration Pathway
  Number represents ∆RF of climate (W m^{-2}) at the end of this century
- GHG mixing ratio time series for CO_2, CH_4, N_2O, as well as CFCs, HCFCs, and HFCs that are provided to climate model groups

Motivation 2



- Prior slide examined atmospheric CO_2 from a single model of the global carbon cycle

- Friedlingstein et al. (2006) compared CO_2 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) difference in CO_2 between a simulation using an interactive carbon-cycle and another run with a non-interactive carbon-cycle varies from 20 to 200 ppm among these **11** models (yikes!)

CO_2 is long lived: society must reduce emissions soon or we will be committed to dramatic, future increases in $[CO_2]$

Curves for which $[CO_2]$ levels off at ~550 ppm or less have emissions peaking NOW !

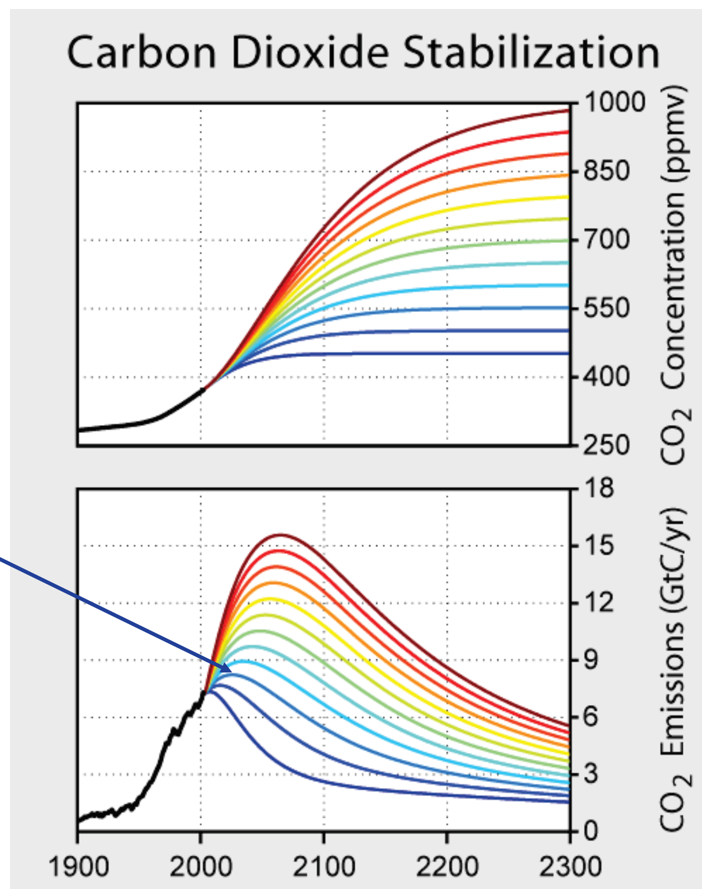
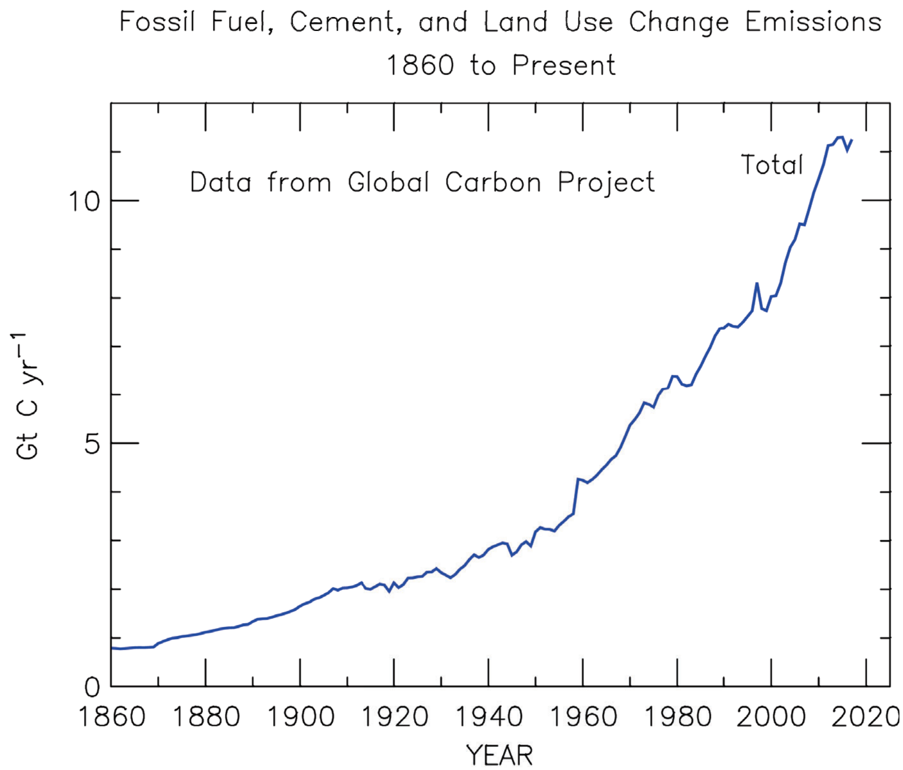


Image: "Global Warming Art" : http://archive.is/JT5rO



Note: Gt is an abbreviation for giga tons, or 10^9 tons. Here we are using *metric tons*:
1 metric ton = 10^3 kg ; therefore, 1 Giga ton = 10^{15} g, where g is grams.

Modern CO_2 Record

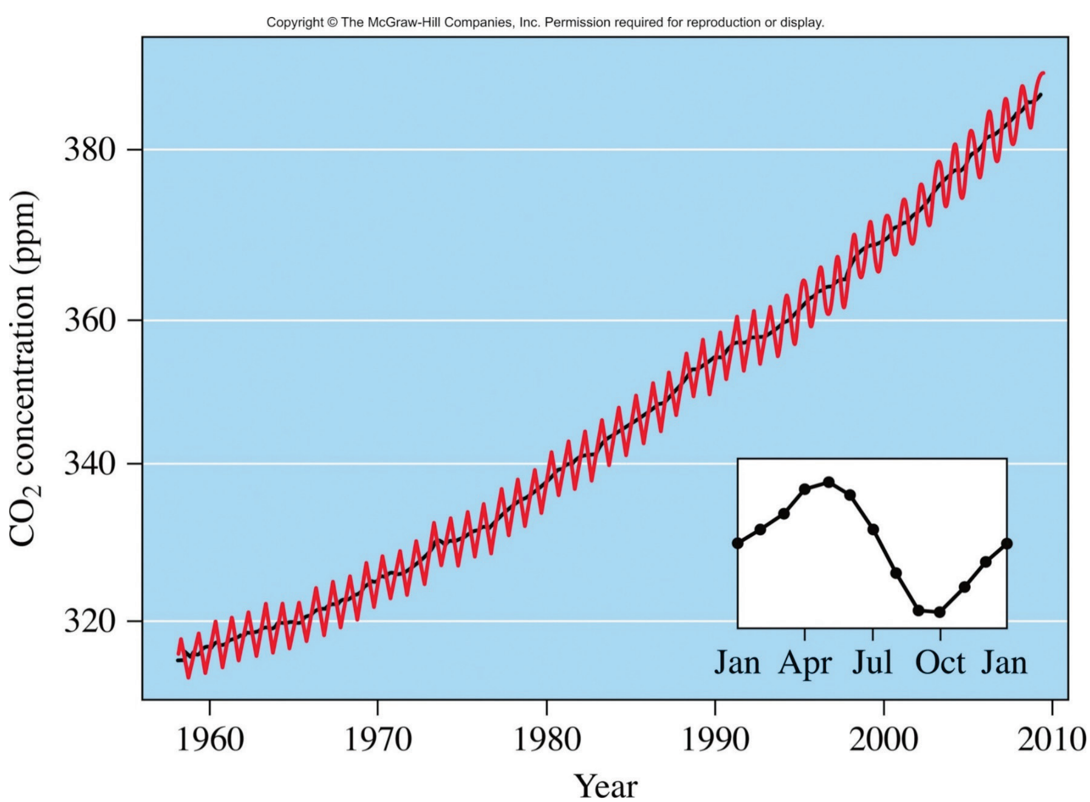
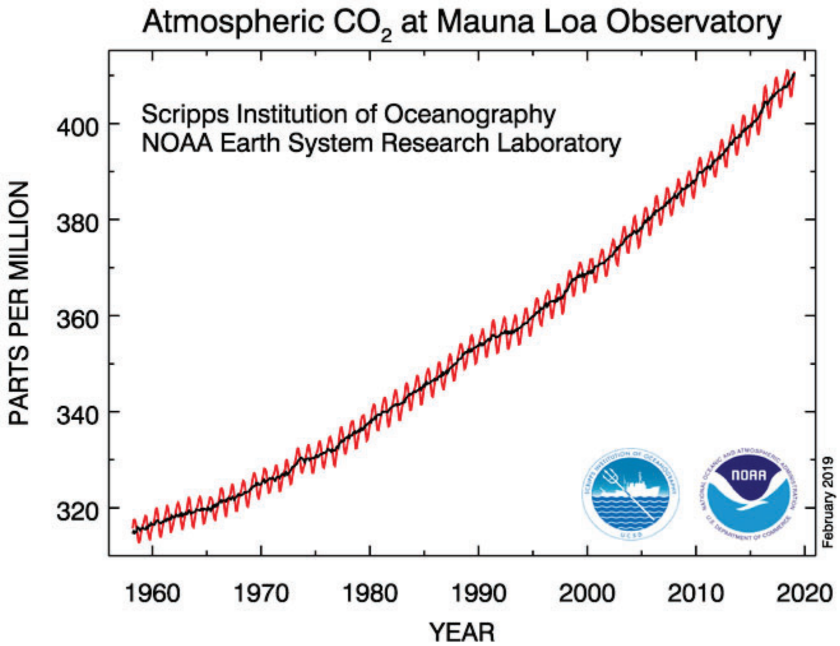


Figure 3.3, Chemistry in Context

Modern CO_2 Record

CO_2 at MLO on 7 Feb 2017: 406.7 parts per million (ppm)
CO_2 at MLO on 12 Feb 2019: 411.8 parts per million (ppm)



Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
https://www.esrl.noaa.gov/gmd/ccgg/trends/full.html
See also https://www.co2.earth/daily-co2

Modern CO_2 Record

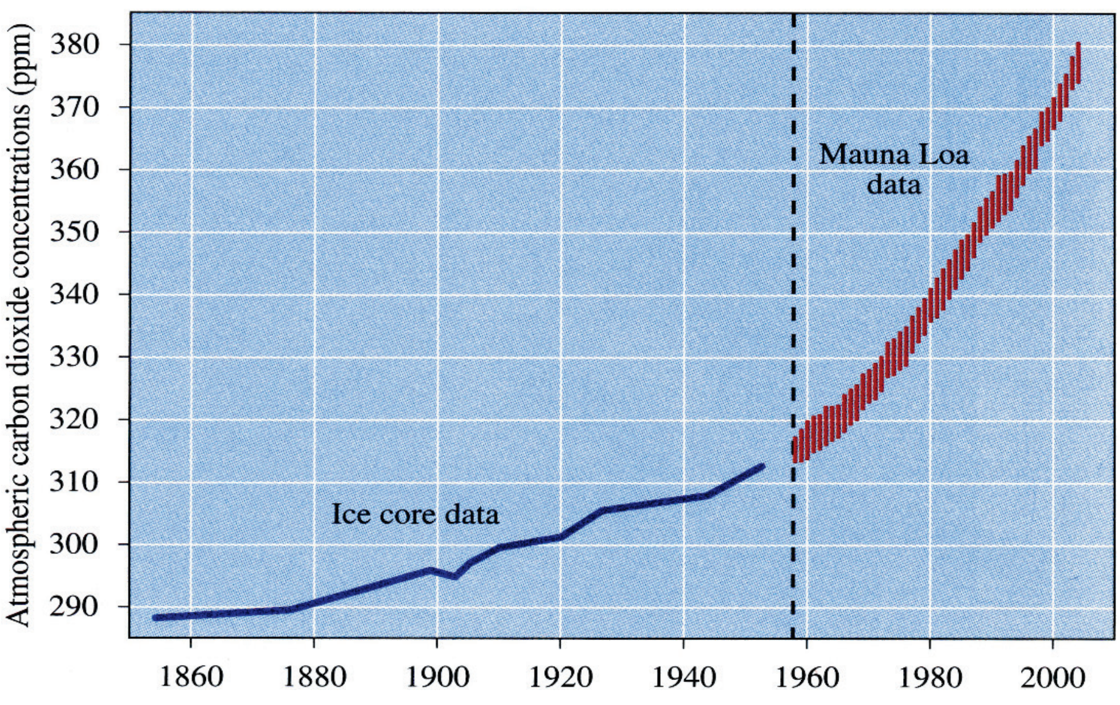
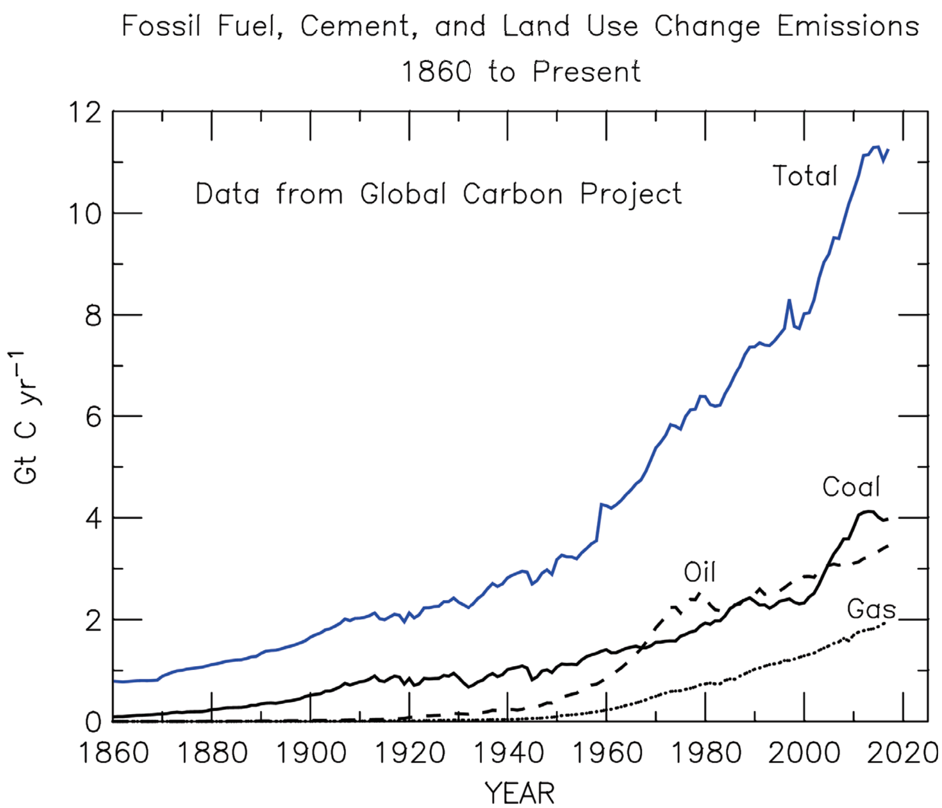


Figure 3.5, *Chemistry in Context, 6th Edition*



Human "Fingerprints" on Atmospheric CO_2

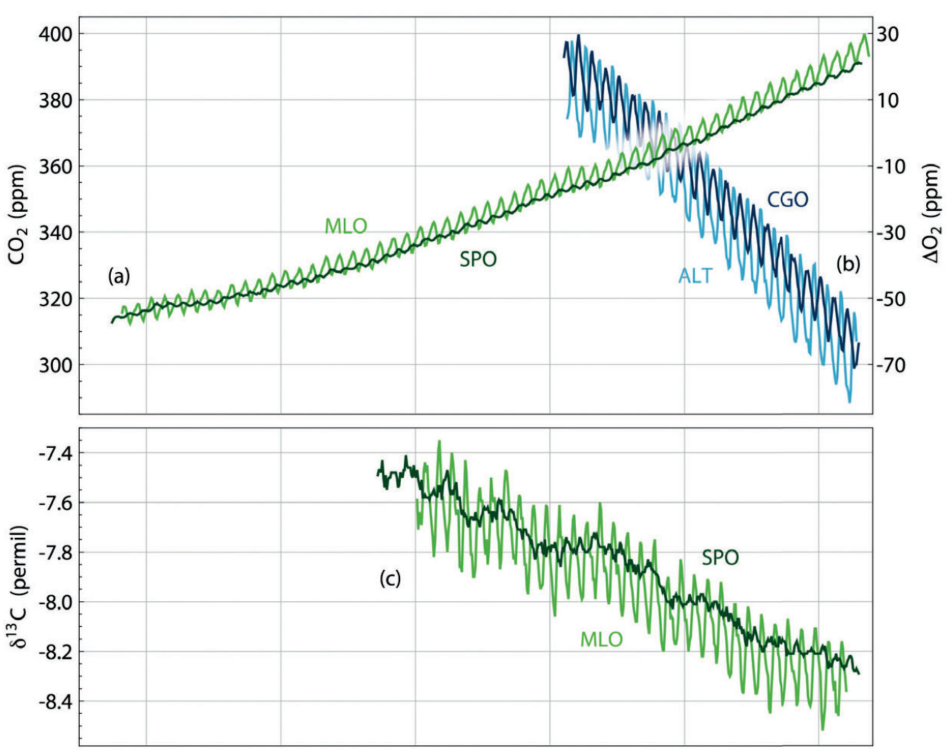
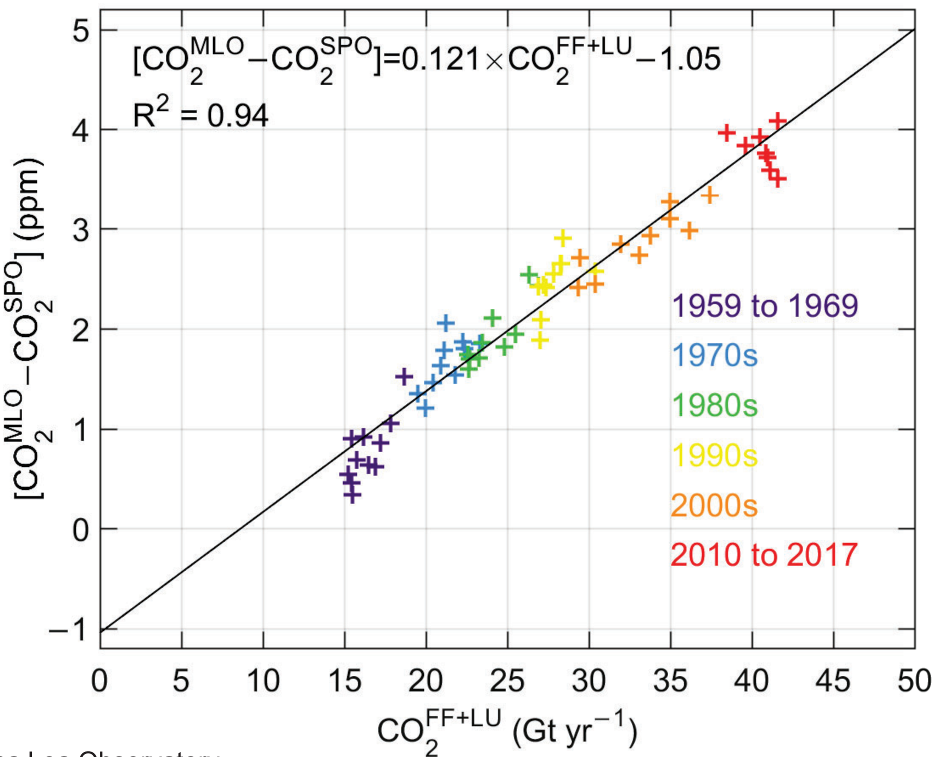


Figure 3.4 Atmospheric concentrations observed at representative stations of (a) carbon dioxide from Mauna Loa (MLO) Northern Hemisphere and South Pole (SPO) Southern Hemisphere; (b) Oxygen from Alert (ALT) Canada, 82°N, and Cape Grim (CGO), Australia, 41°S; (c) $^{13}C/^{12}C$ from Mauna Loa (MLO) and South Pole (SPO) stations.

Fig 3.4, Houghton

Human "Fingerprints" on Atmospheric CO_2



MLO: Mauna Loa Observatory
SPO: South Pole Observatory

Fig 1.8 updated, *Paris Beacon of Hope*

Note, here we use Gt C, whereas in the book, we used GT CO_2

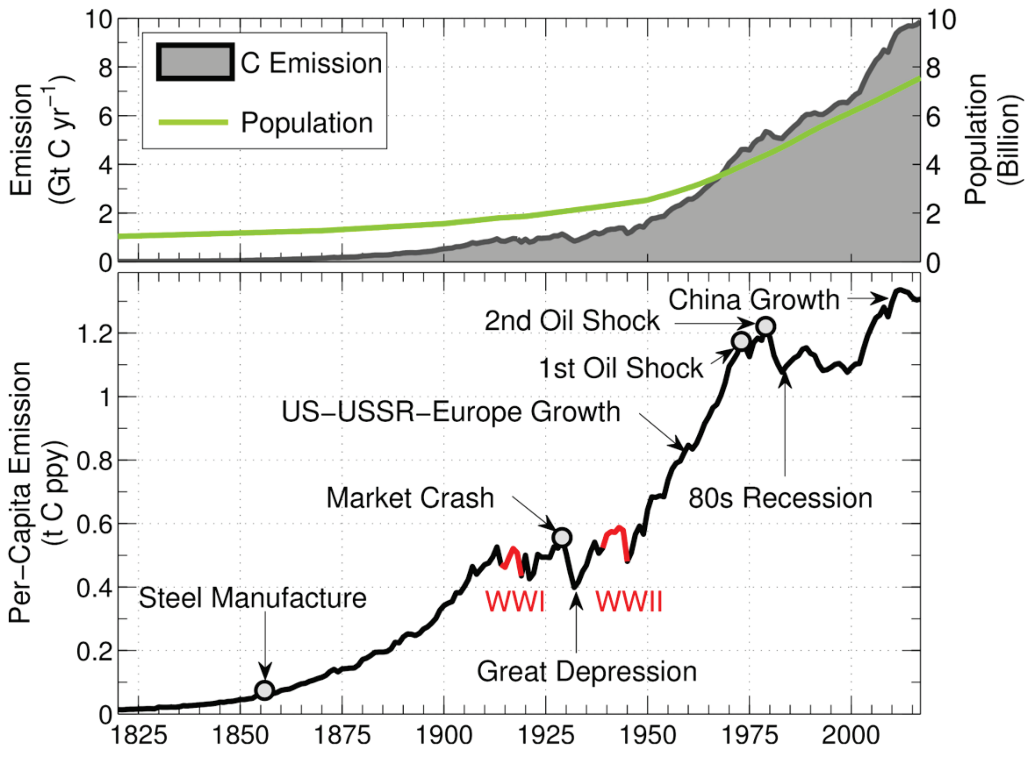
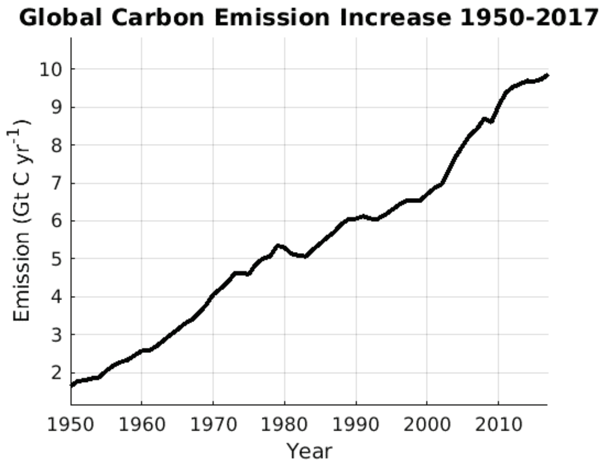


Figure courtesy Walt Tribett

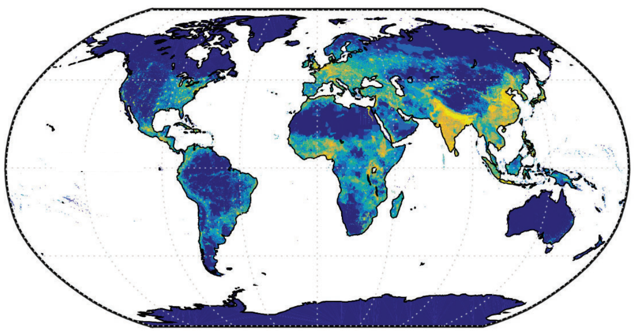
After Fig 3.1 *Paris Beacon of Hope*

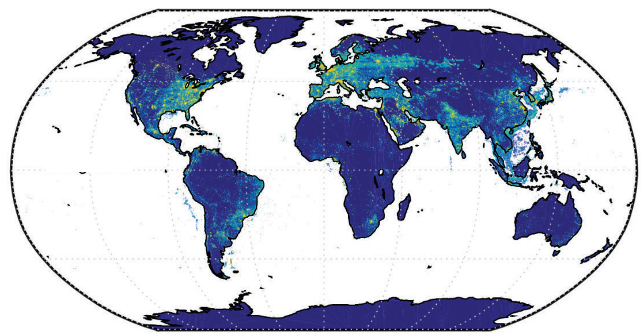
Fossil Fuel Emissions



Fossil fuel emissions, 1950 = **1.6** Gt C
2017 = **9.9** Gt C

What are the primary social factors driving factors responsible for this rise?

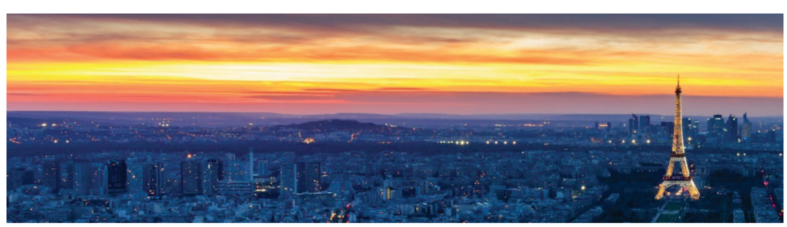




Obama & Xi

US / China Announcement ⇒ Paris Climate Agreement

Nov 2014: Presidents Obama & Xi announced
- **U.S. would reduce GHG emissions to 27% below 2005 by 2025**
- **China would peak GHG emissions by 2030 with best effort to peak early**

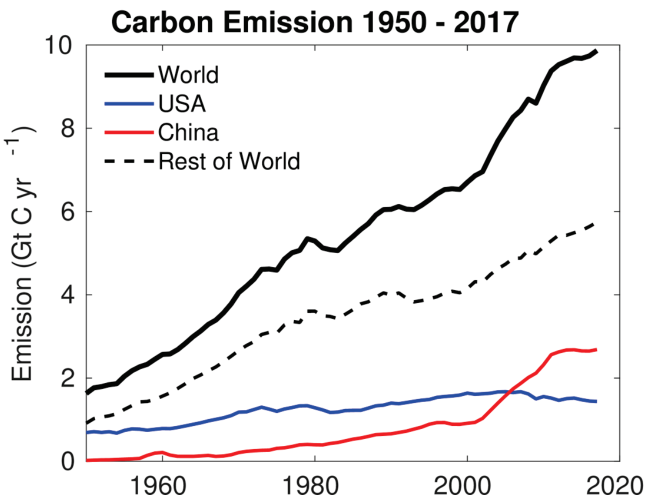


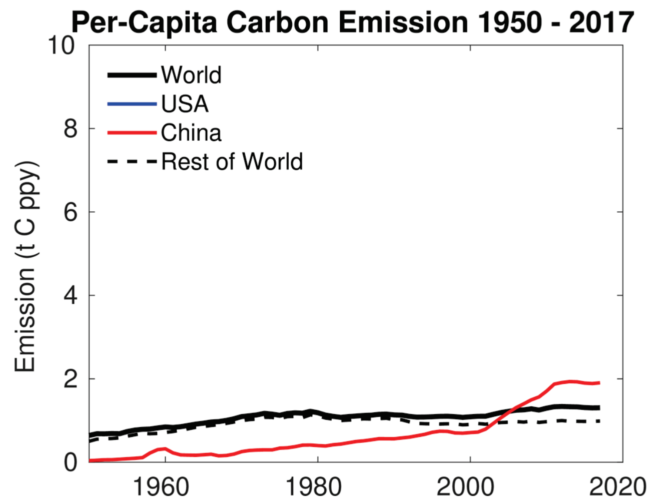
Paris Climate Agreement:

Article 2, Section 1, Part a):

Objective to hold "increase in GMST to well below **2°C** above pre-industrial levels and to pursue efforts to limit the temperature increase to **1.5°C** above pre-industrial levels"

NDC: **N**ationally **D**etermined **C**ontributions to reduce GHG emissions
- Submitted prior to Dec 2015 meeting in Paris
- Consist of either **unconditional** (promise) or **conditional** (contingent) pledges
- Generally extend from early 2016 to year 2030





Figures courtesy Walt Tribett

Global Carbon Cycle

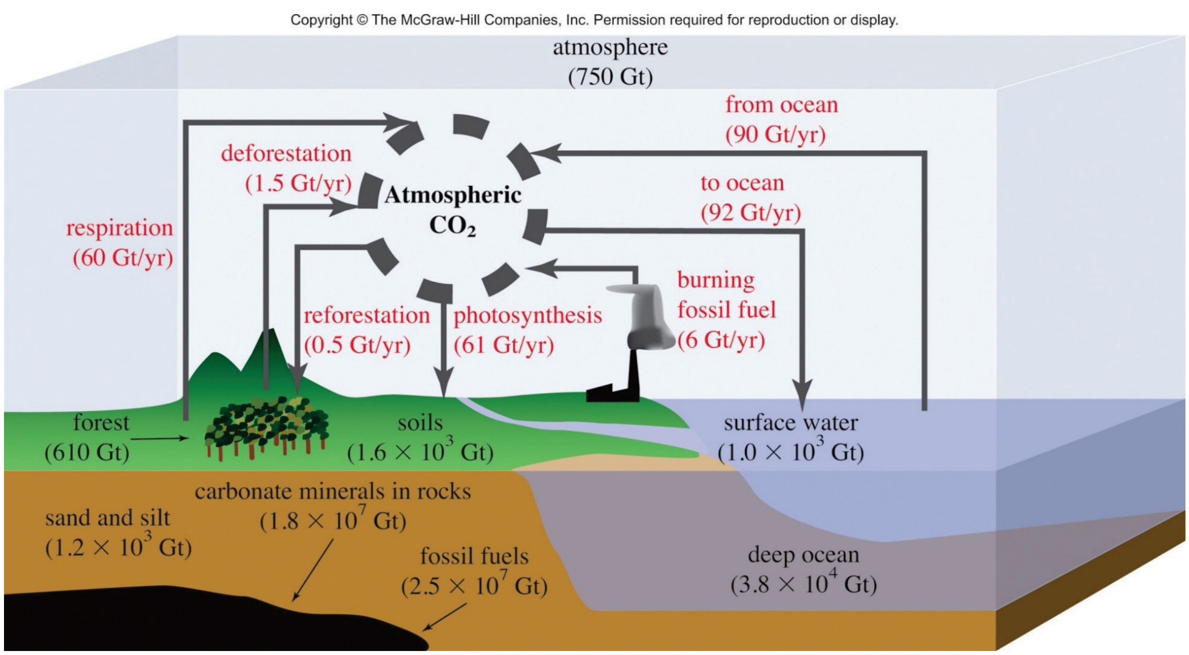


Fig 3.20, Chemistry in Context

Ocean Carbon: 1.0×10^3 Gt + 3.8×10^4 Gt = 3.9×10^4 Gt

Ocean contains ~50 times more Carbon than the atmosphere

Mass of C (in CO_2) = $409.5 \times 10^{-6} \times 5.27 \times 10^{21}$ grams × { (12 grams/mole) / (28.8 grams/mole) }
= 899×10^{15} grams or 899 Gt

Note: 1 Pg (peta g) is 10^{15} g exactly the same as 1 Gt

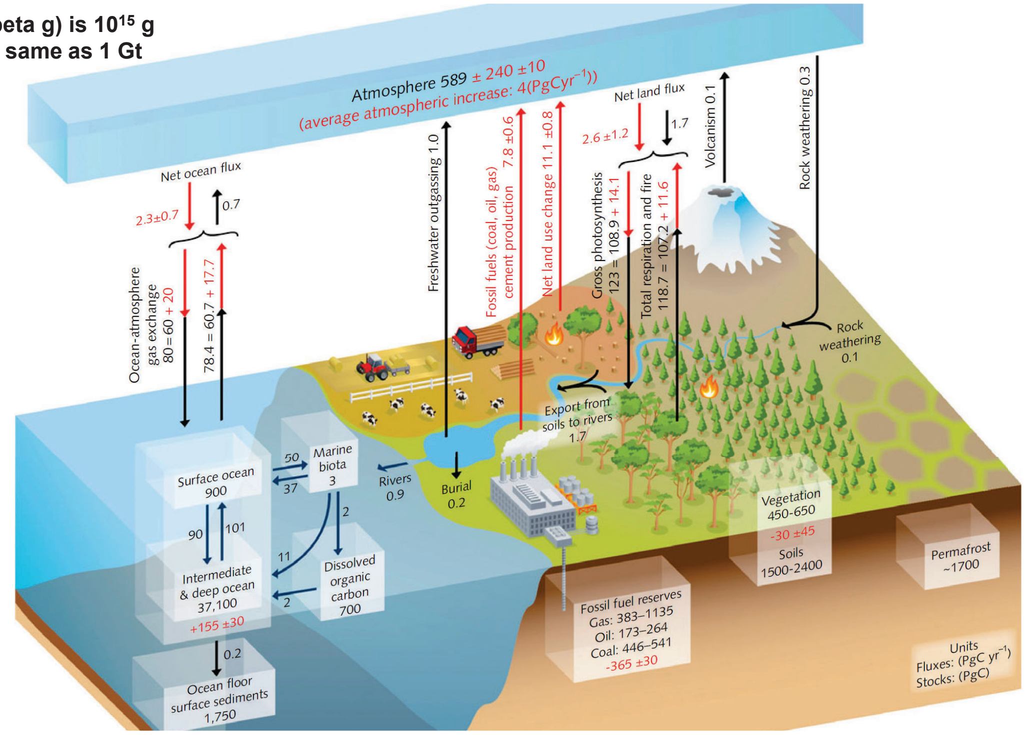


Fig 3.1, Houghton

Houghton:

Land Sink	**= 2.6 ± 1.2 Gt C / yr**
Ocean Sink	**= 2.3 ± 0.7 Gt C / yr**

In other words, ~4.9 Gt C / yr out of 7.8 + 1.1 = 8.9 Gt C / yr from burning fossil fuel & deforestation is being absorbed by world's oceans & terrestrial biosphere for the time period of this figure, which is 2000 to 2009

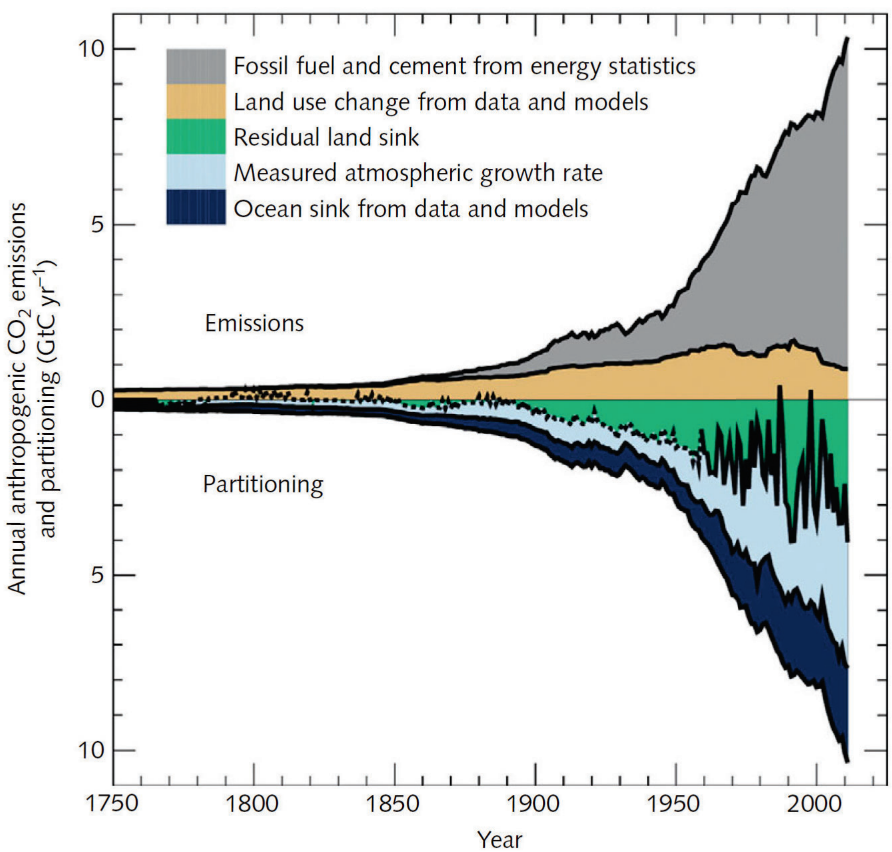
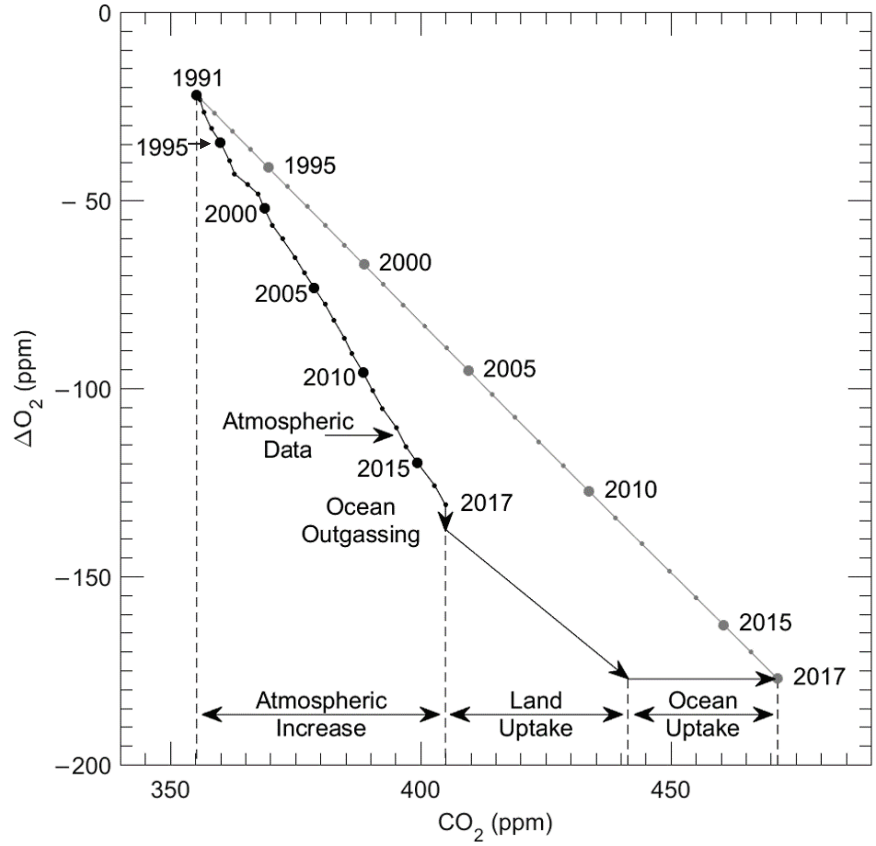


Fig 3.3, Houghton

Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



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 could lead to almost 100 ppm additional CO_2 by end of century

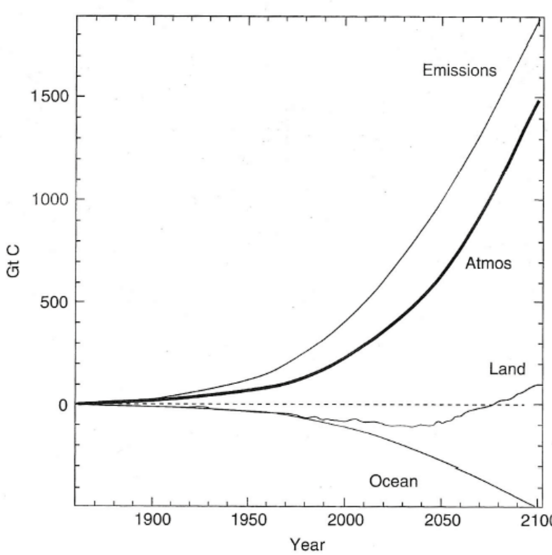
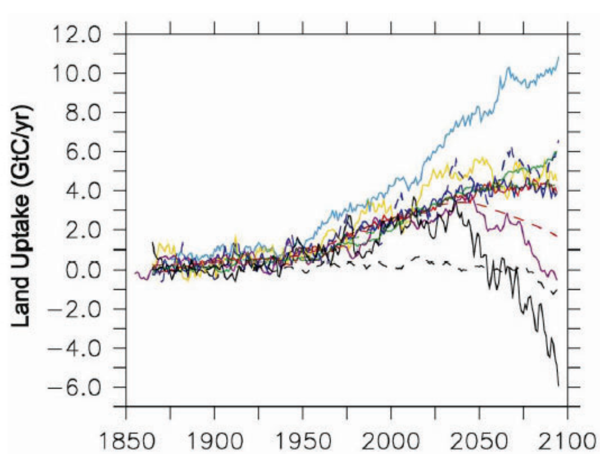


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbo cycle. Results are shown of the changing budgets of carbon

Page 41, Houghton

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

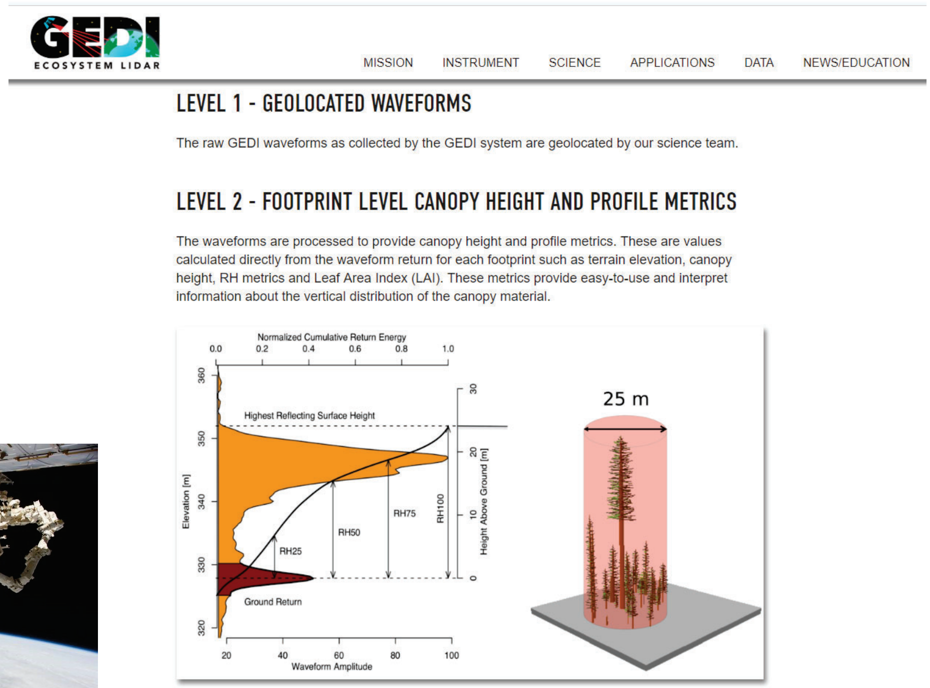


Uptake of Atmospheric CO_2 by Trees (Land Sink)

Land sink

Recently launched instrument will use a lidar to map global vegetation

GEDI: Global Ecosystem Dynamics Investigation



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 could lead to almost 100 ppm additional CO_2 by end of century

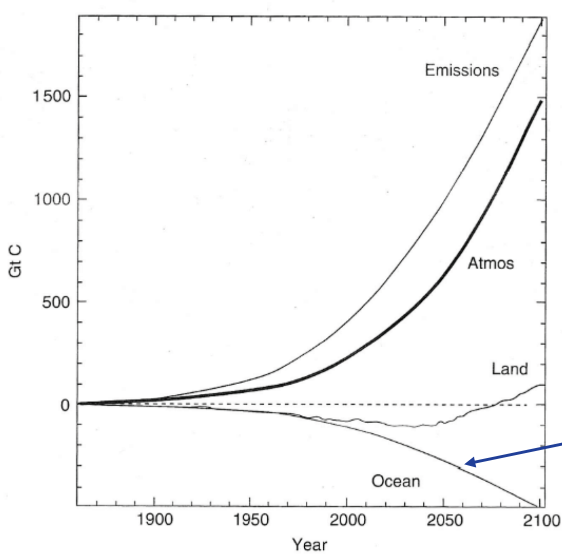


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

Figure 3.5, Houghton 3d Edition

Ocean sink: relatively long lived reservoir

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

Biology in Today's Ocean

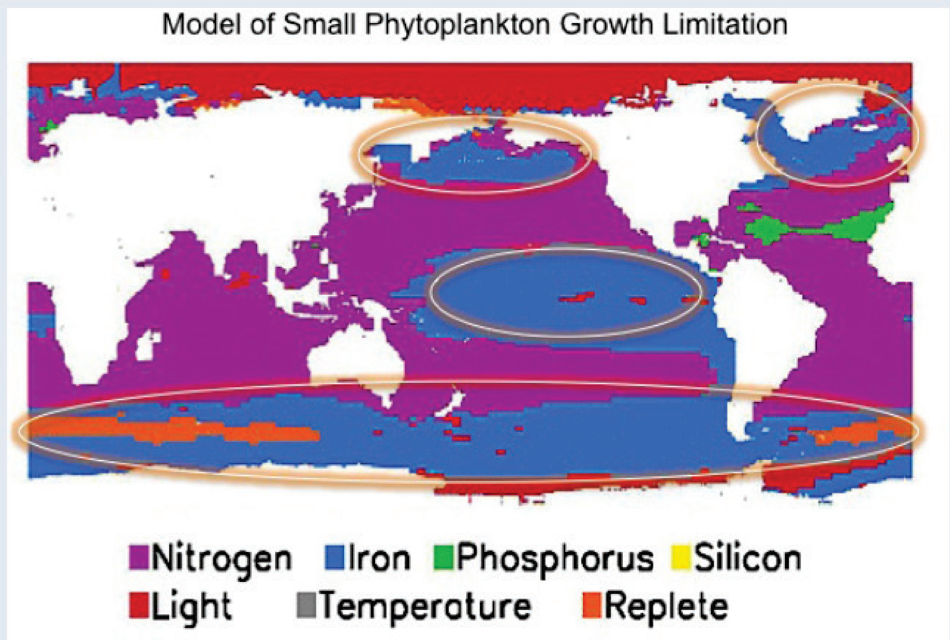
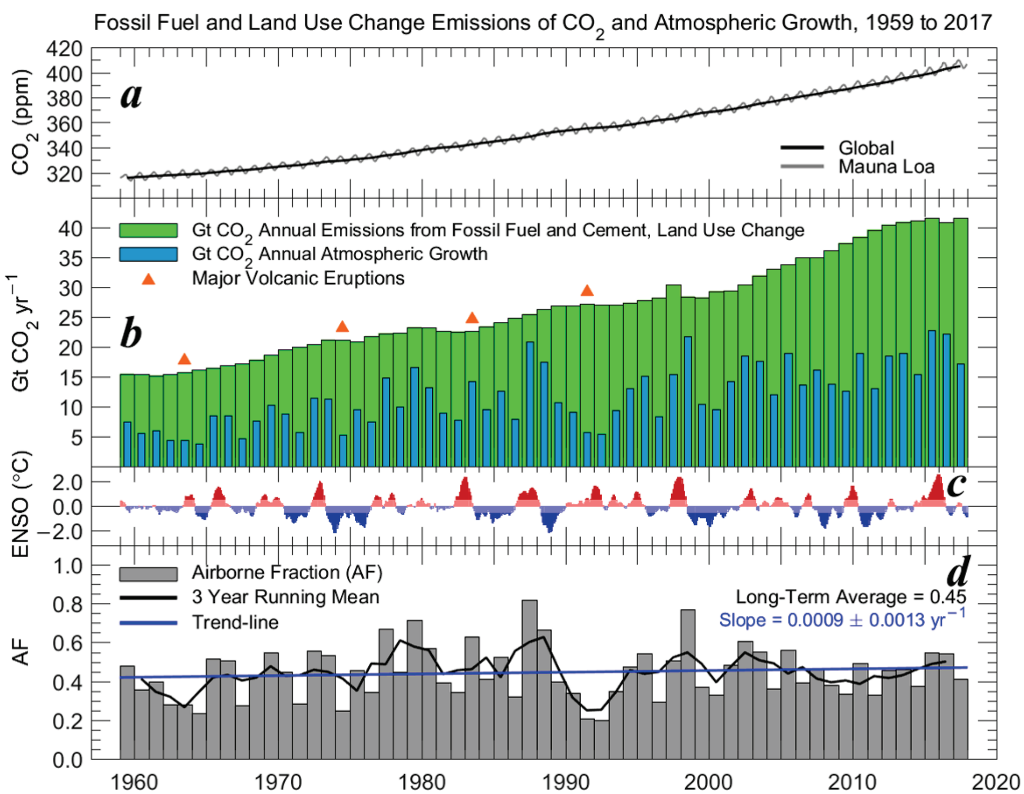


Figure 1. Results of a global model of small phytoplankton growth limitation by Moore et al. 2004 (*Global Biogeochemical Cycles*). Blue shaded areas denote regions that are potentially limited by iron availability. Iron is supplied by dust from continents and by upwelling of deep water. However, high 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



Airborne Fraction (AF) is the ratio of the increase in the mass of atmospheric CO_2 divided by the total mass of carbon emitted to the atmosphere, in this case over annual time periods

Fig 1.6 (updated & modified), *Paris Beacon of Hope*

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	260 ppm Pre-Industrial	409 ppm Present Day	520 ppm 2 × Pre-Indus.
Ocean Carbon	2007×10^{-6} M	2079×10^{-6} M	2112×10^{-6} M
$[HCO_3^-]$	1748×10^{-6} M	1881×10^{-6} M	1941×10^{-6} M
$[CO_2\,(aq)]$	8.47×10^{-6} M	13.3×10^{-6} M	16.9×10^{-6} M
$[CO_3^{2-}]$	251×10^{-6} M	188×10^{-6} M	155×10^{-6} M
pH	8.34	8.18	8.09

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

Notes:

T = 293 K; Alkalinity= 2.25×10^{-3} M

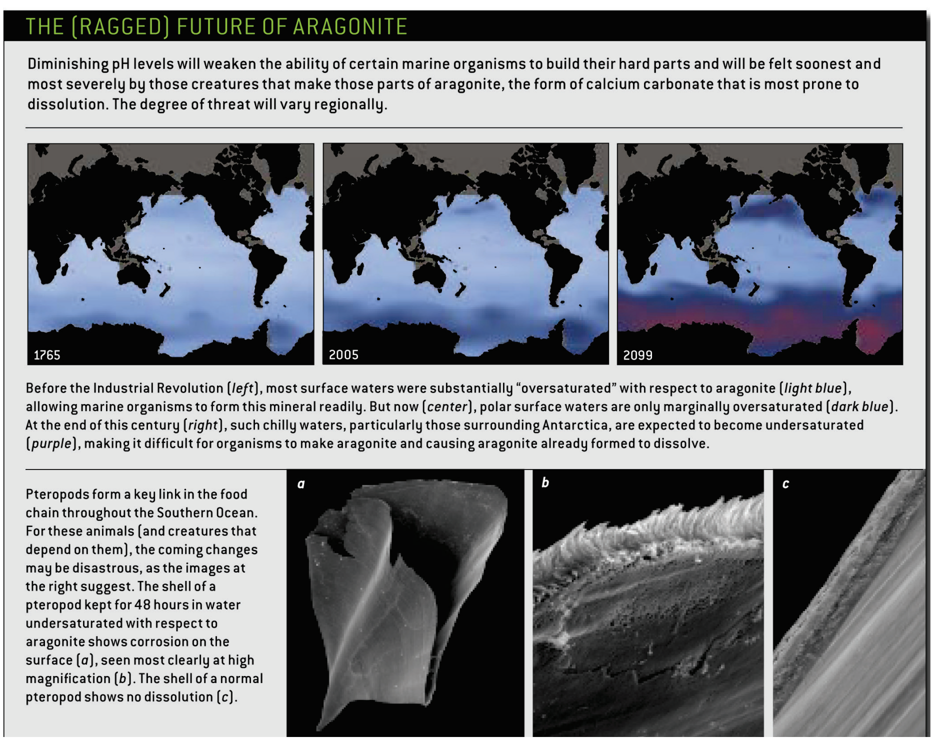
M ≡ mol/liter

Mathematics supporting this calculation on Extra Slides 1 to 3

Uptake of Atmospheric CO_2 by Oceans

Oceanic uptake of atmospheric CO_2 leads to ***ocean acidification***

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



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

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	260 ppm Pre-Industrial	409 ppm Present Day	520 ppm 2 × Pre-Indus.
Ocean Carbon	2007×10^{-6} M	2079×10^{-6} M	2112×10^{-6} M
$[HCO_3^-]$	1748×10^{-6} M	1881×10^{-6} M	1941×10^{-6} M
$[CO_2\,(aq)]$	8.47×10^{-6} M	13.3×10^{-6} M	16.9×10^{-6} M
$[CO_3^{2-}]$	251×10^{-6} M	188×10^{-6} M	155×10^{-6} M
pH	8.34	8.18	8.09

$$\frac{\Delta \text{Atmos}_{CO2}}{\langle \text{Atmos}_{CO2} \rangle_{AVERAGE}} = \frac{149 \text{ ppm}}{0.5 \times (409 + 260) \text{ ppm}} = 0.45$$

$$\frac{\Delta \text{Ocean Carbon}}{\langle \Delta \text{Ocean Carbon} \rangle_{AVERAGE}} = \frac{72 \times 10^{-6} \text{ M}}{0.5 \times (2007 + 2079) \times 10^{-6} \text{ M}} = 0.035$$

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	260 ppm Pre-Industrial	409 ppm Present Day	520 ppm 2 × Pre-Indus.
Ocean Carbon	2007×10^{-6} M	2079×10^{-6} M	2112×10^{-6} M
$[HCO_3^-]$	1748×10^{-6} M	1881×10^{-6} M	1941×10^{-6} M
$[CO_2\,(aq)]$	8.47×10^{-6} M	13.3×10^{-6} M	16.9×10^{-6} M
$[CO_3^{2-}]$	251×10^{-6} M	188×10^{-6} M	155×10^{-6} M
pH	8.34	8.18	8.09

$$\frac{\Delta \text{Atmos}_{CO2}}{\langle \text{Atmos}_{CO2} \rangle_{AVERAGE}} = \frac{111 \text{ ppm}}{0.5 \times (520 + 409) \text{ ppm}} = 0.23$$

$$\frac{\Delta \text{Ocean Carbon}}{\langle \Delta \text{Ocean Carbon} \rangle_{AVERAGE}} = \frac{33 \times 10^{-6} \text{ M}}{0.5 \times (2079 + 2112) \times 10^{-6} \text{ M}} = 0.015$$

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	260 ppm Pre-Industrial	409 ppm Present Day	520 ppm 2 × Pre-Indus.
Ocean Carbon	2007×10^{-6} M	2079×10^{-6} M	2112×10^{-6} M
$[HCO_3^-]$	1748×10^{-6} M	1881×10^{-6} M	1941×10^{-6} M
$[CO_2\,(aq)]$	8.47×10^{-6} M	13.3×10^{-6} M	16.9×10^{-6} M
$[CO_3^{2-}]$	251×10^{-6} M	188×10^{-6} M	155×10^{-6} M
pH	8.34	8.18	8.09

Revelle Factor:

Although the oceans presently take up about one-fourth of the excess CO_2 human activities put into the air, that fraction was significantly larger at the beginning of the Industrial Revolution. That's for a number of reasons, starting with the simple one that as one dissolves CO_2 into a given volume of seawater, there is a growing resistance to adding still more CO_2

https://scripps.ucsd.edu/programs/keelingcurve/2013/07/03/how-much-co2-can-the-oceans-take-up

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 ?

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

For CO_2 = 390 ppm:

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

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

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

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

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

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

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

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

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

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

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

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

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

where Alk stands for Alkalinity

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

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

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

If we substitute $[HCO_3^-] = Alk - 2\,[CO_3^{2-}]$ into the eqn above, we arrive at a quadratic eqn for $[CO_3^{2-}]$ as a function of pCO_2 and Alk. Note that α, K_1, and 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 $[CO_3^{2-}]$ from the quadratic eqn.

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

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

Numerical values on the slides entitled "Uptake of Atmospheric CO_2 by Oceans" were found in this manner, using Fortran program http://www.atmos.umd.edu/~rjs/class/code/ocean_carbon.f