Global Carbon Cycle

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2020
https://myelms.umd.edu/courses/1291919

Goals for today:

- **Overview of the Global Carbon Cycle "scratching below the surface"**
- **Ocean and land uptake of CO_2 : past and future**
- **Policy to reduce emissions of CO_2**

Lecture 5

17 September 2020

Announcements: Class

1) Problem Set 1 posted:

- please email me with questions, concerns, difficulties getting started, etc
- students in 433 have one assignment; students in 633 have a different assignment

2) Lecture material available on-line will reflect what is actually shown in class

09/15	Climates of the Past	Chemistry in Context, Sec 2.2, 3.0, 3.1, 3.2 (14 pages) Houghton, Ch 4 (pgs 77-84) Paris Beacon of Hope Sec 1.1 (7 pages; please review)	AT 4	Lecture 4 2020 Zoom Video		Chylek & Lohmann, GRL, 2008 * IPCC 2007 FAQ (questions 6.1, 6.2) Parrenin et al., Science, 2013 Press release for Sept 2020 paper	Quiz 4
09/17	Global Carbon Cycle	Chemistry in Context, Sec 3.5, 4.0, 4.1, 6.5 (8 pages) Houghton, Pg 33-46 Paris Beacon of Hope Sec 1.2.3.2 (8 pages)	AT 5	Lecture 5 2020 Zoom Video		IPCC 2007, Section 7.3.4.1 & Box 7.3 * Doney, Ocean Acidification, *Scientific American*, March 2006 Global Carbon Project	Quiz 5
09/22	Biogeochemical Cycles of CH_4 and N_2O	Chemistry in Context, Sec 3.8 & Sec 6.9 (8 pages) Houghton, Pg 46-50 Paris Beacon of Hope Sec 1.2.3.3 & 1.2.3.4 (5 pages)	AT 6	Lecture 6 2020 Zoom Video	**Problem Set 1 due today:** **433 Students** **633 Students**	Kirschke et al., 2013 * Kort et al., 2014 Saunois et al., 2019	Quiz 6

Different URLs

https://www2.atmos.umd.edu/~rjs/class/fall2020

Announcements: Class

1) Problem Set 1 posted:

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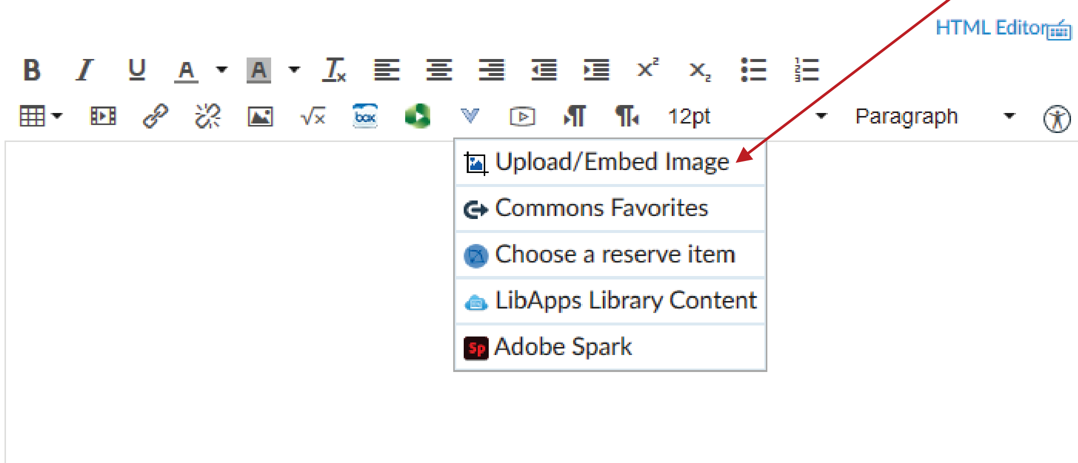
Compare the two effective temperatures found in a) and c), and state whether:

i) the difference is physically consistent with the answer you expect, given the direction of the change in albedo

ii) your calculations support the notion that loss of sea-ice is an ***important concern*** as a "feedback" (i.e., amplification) for the warming of climate due to rising levels of greenhouse gases (GHGs)

As you formulate a reply you might want to review the paragraph on climate feedback at the end of FAQ 1.1 of this Lecture 2 reading: as well as graphs shown the global mean surface temperature shown in numerous places during Lecture 2 before formulating your reply.

a) Please answer all questions within ELMS
b) Please "show your work"
c) Either writing in text box OR uploading a file (scan of written work) is fine; this V symbol allows scanned images to be uploaded.



Announcements: Outside of Class

1) Thurs, 17 Sept : AOSC Weekly Seminar (Today at 3:30 pm)

Professor Don Milton, University of Maryland

Infectious Drops and Aerosols

We will review modes of respiratory virus transmission, the history of thinking about modes of transmission and the role of aerosols in the medical community, and the problem with vague terminology and ensuing confusion and miscommunication. We will then review evidence from observational and experimental studies of influenza and SARS-CoV-2 and talk about future plans to resolve the key questions.

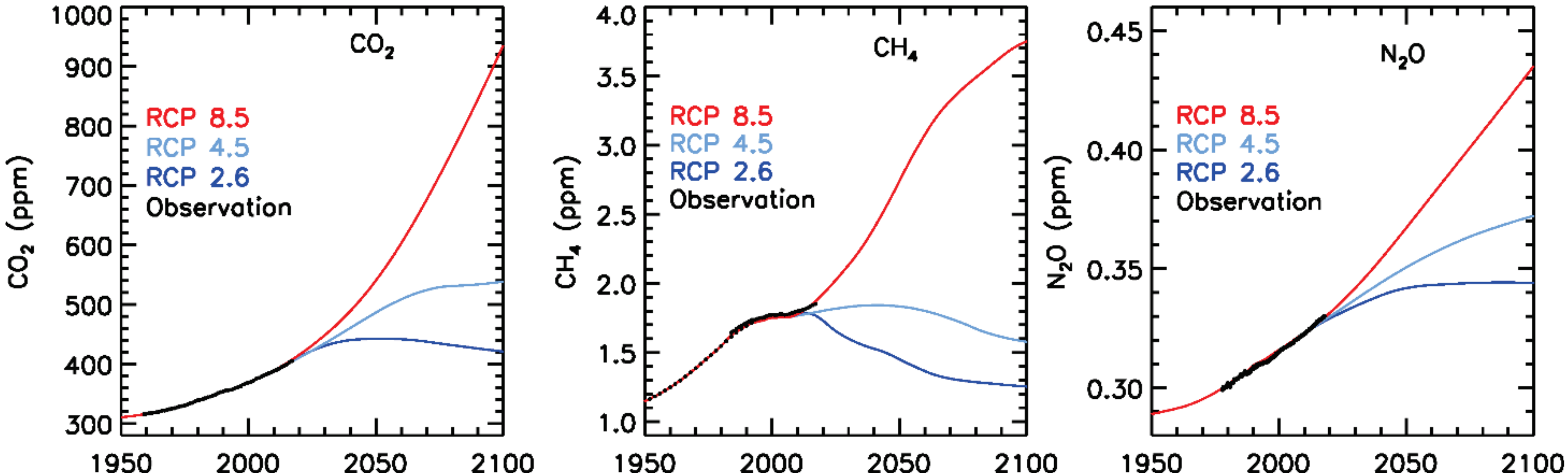
https://aosc.umd.edu/seminars/department-seminar

Email Joseph Knisely at jknisely@umd.edu for Zoom connection info

For today, since time is tight:

https://umd.zoom.us/j/94562248135?pwd=TEIyVS9TY0ZTSTZZNU01L0F1eTdTZz09

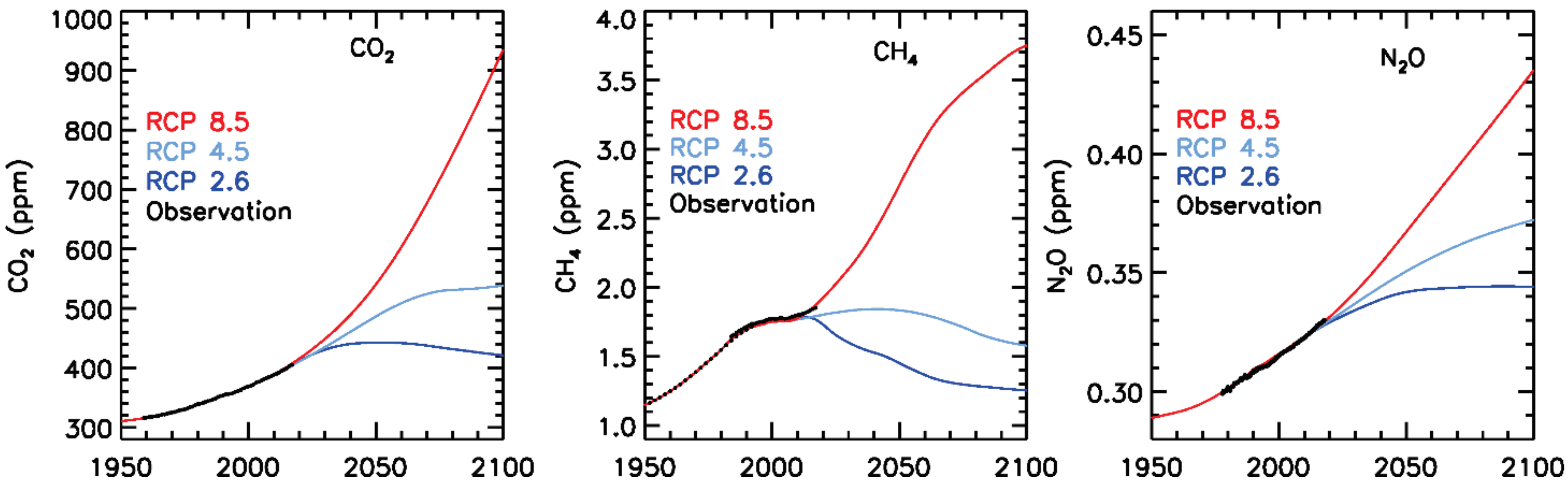
Motivation 1



- RCP: Representative Concentration Pathway
  Number represents ΔRF 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

Figure from Hope et al., 2020: https://www.essoar.org/pdfjs/10.1002/essoar.10504179.1

Motivation 1



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

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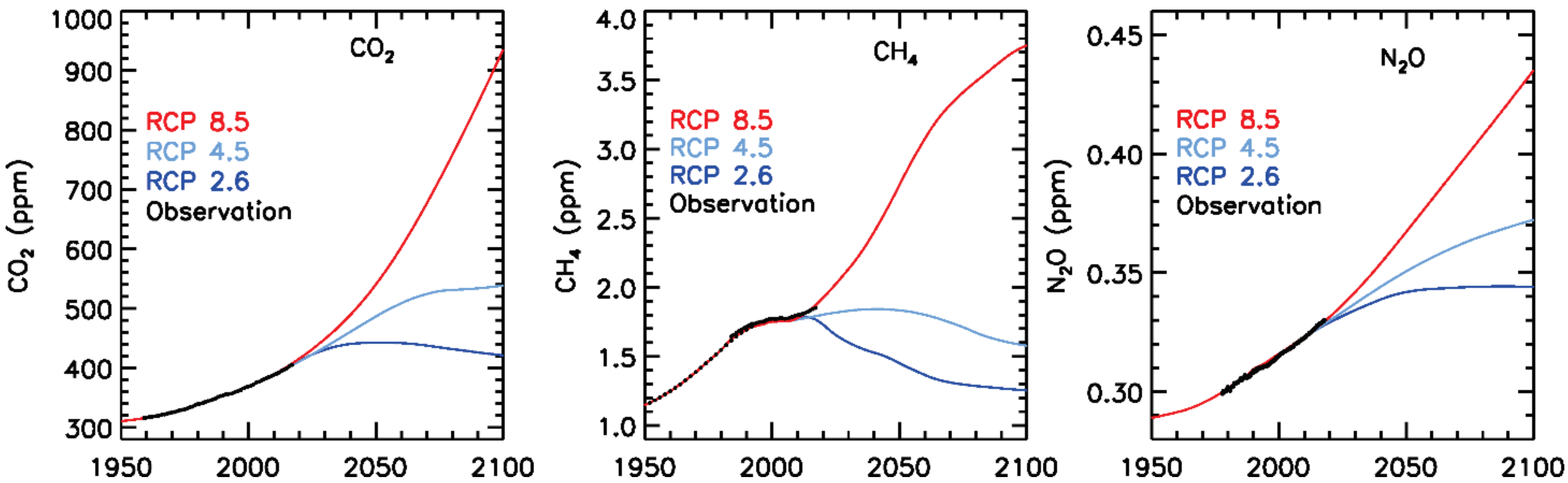
Motivation 1



- RCP: Representative Concentration Pathway
  Number represents ΔRF 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
- What is the utility of "command central" providing GHG scenarios to the climate model groups?
- How do you think these various scenarios are devised?

Figure from Hope et al., 2020: https://www.essoar.org/pdfjs/10.1002/essoar.10504179.1

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 !

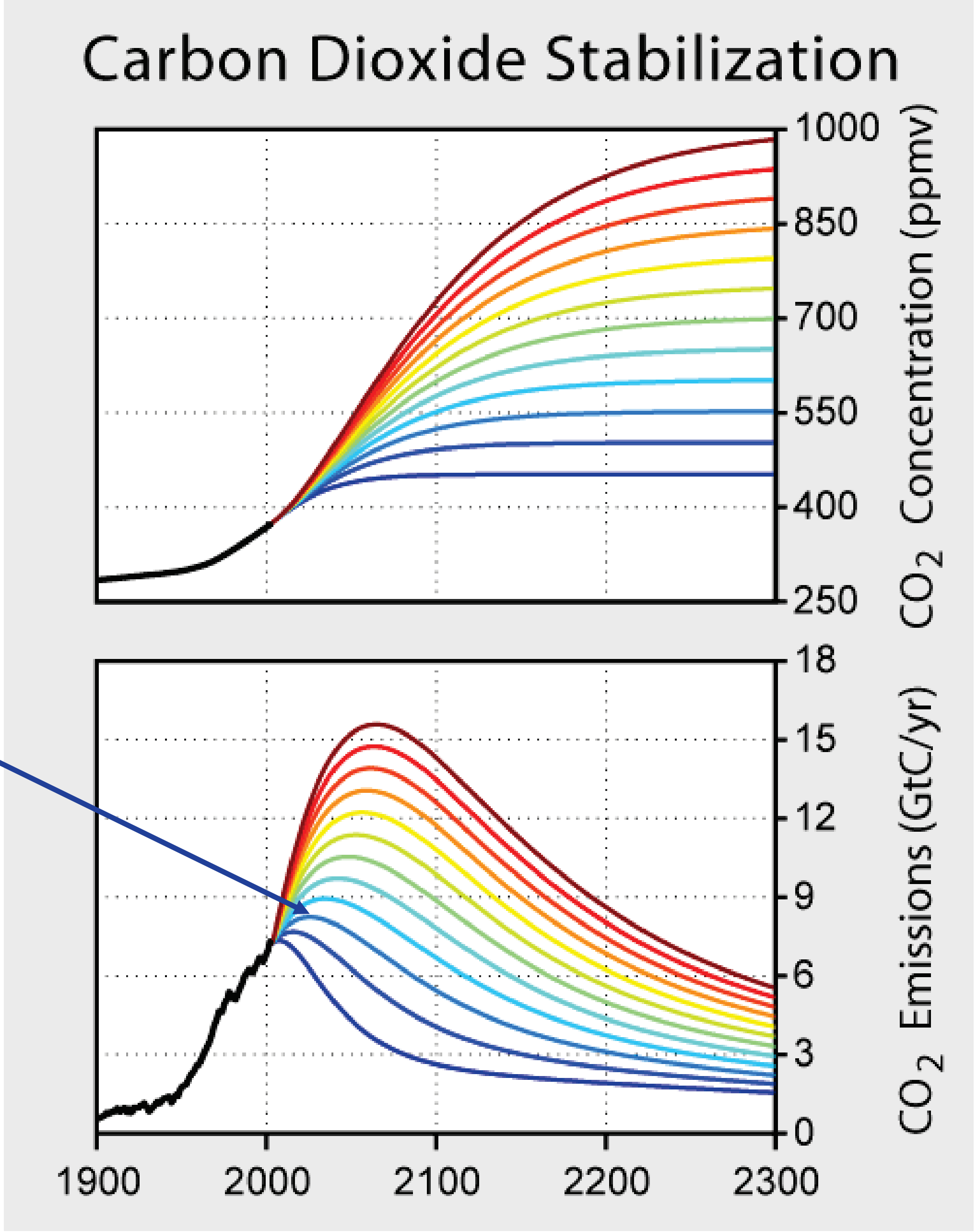
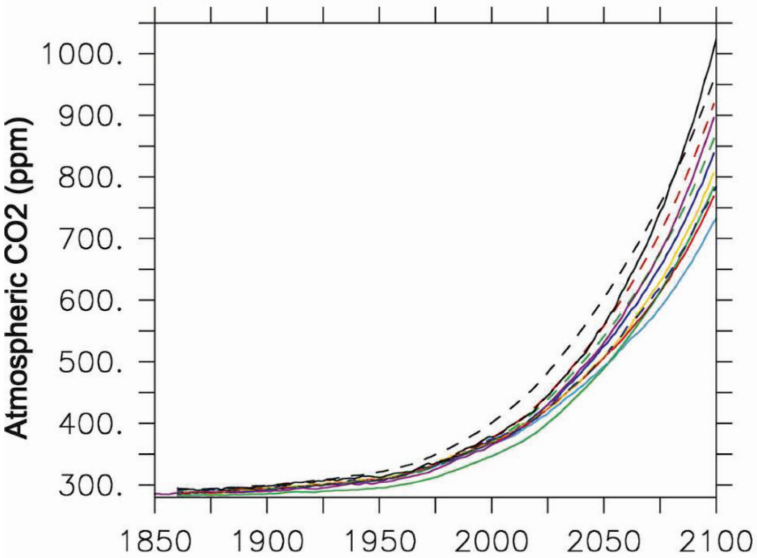
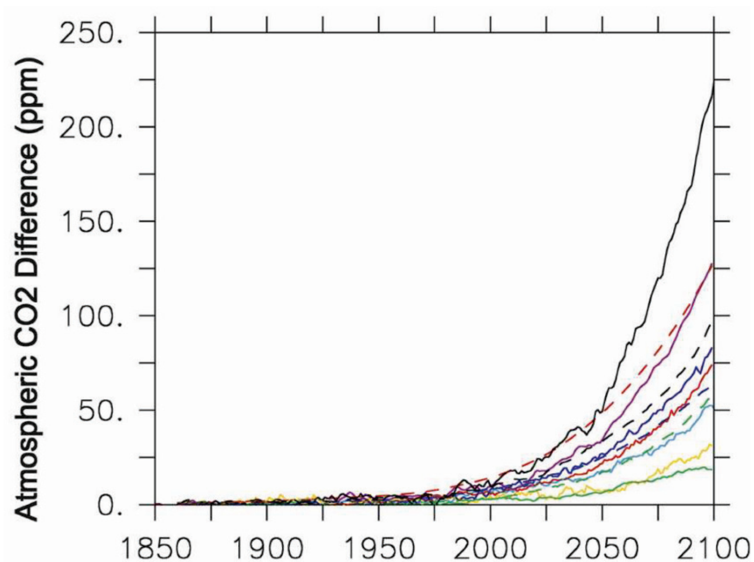


Image: "Global Warming Art" : http://archive.is/JT5rO

Motivation 2



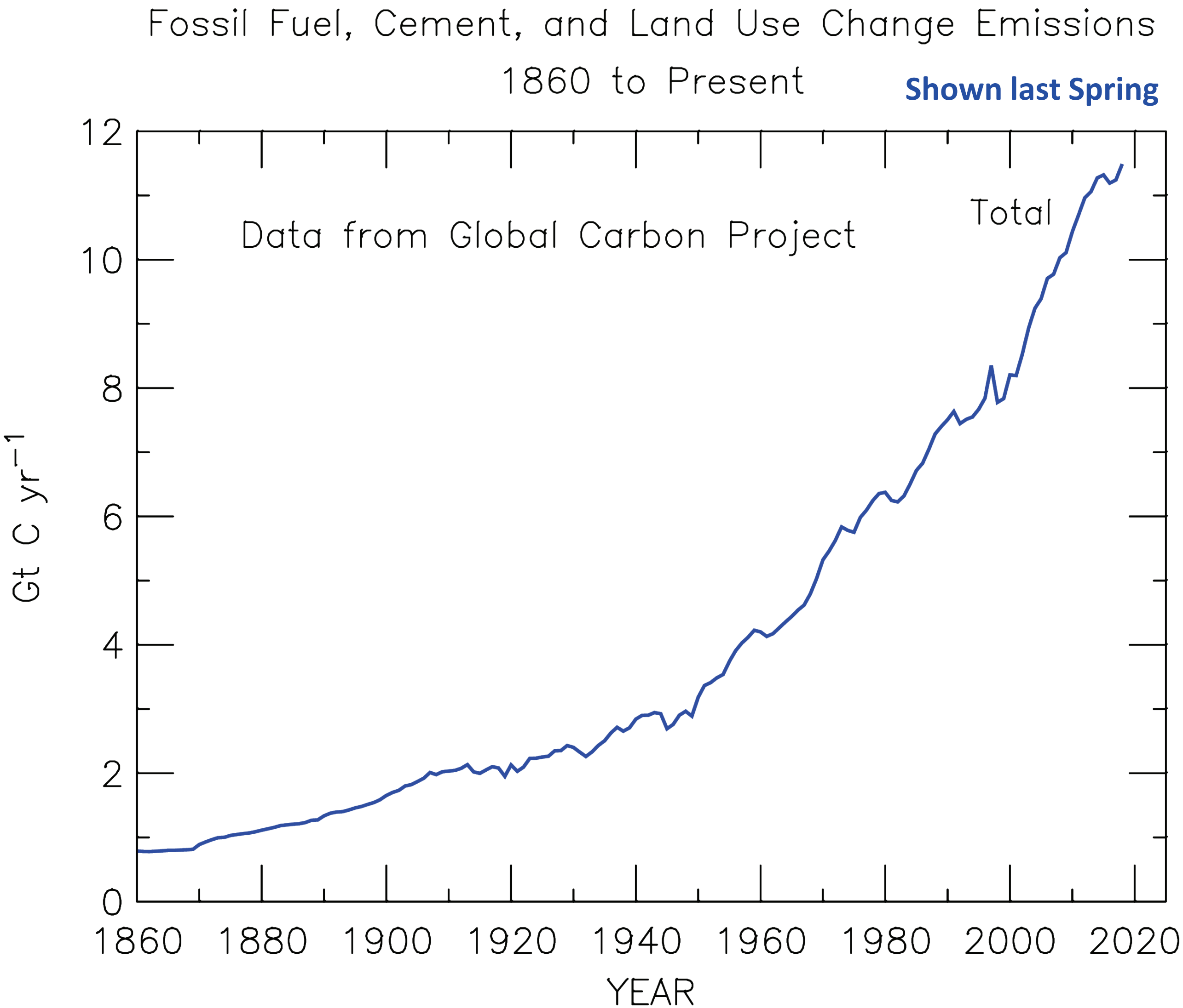


- Prior slides examined atmospheric CO_2 from a single model of the global carbon cycle

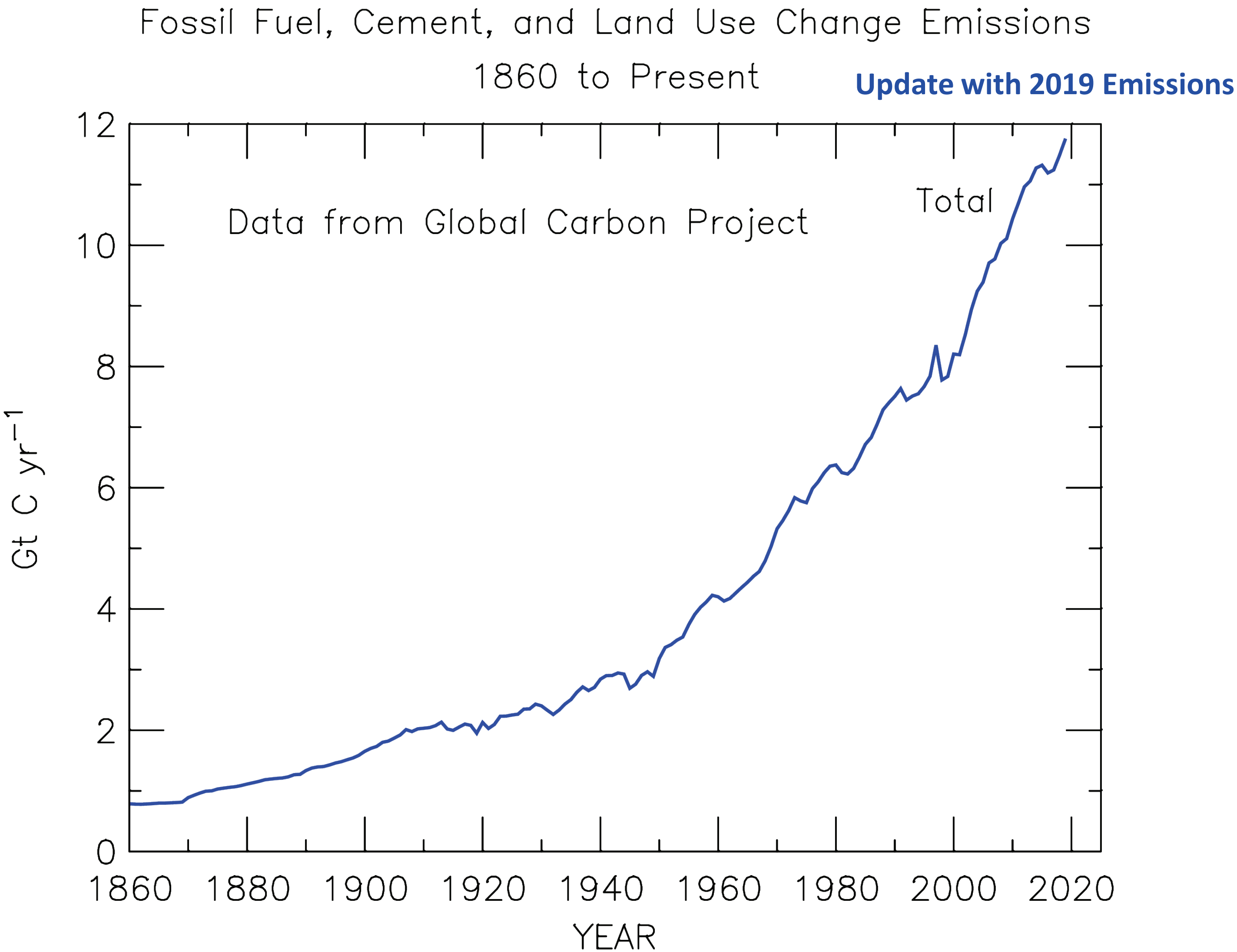
- Friedlingstein et al. (2006) compared CO_2 from **11** different coupled climate-carbon cycle models, each constrained by the *same* specified time series of anthropogenic CO_2 emission and found:

    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!)



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.



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Human Release of Carbon

Human activity is presently releasing more than 12 Gt (giga tons) or 12×10^9 (12,000,000,000) tons of carbon into the atmosphere every year.

How much is 12 Gt of carbon ?!?

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Mazda Miata weighs about 1 ton (2200 lbs)

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12 Gigatons C $\approx$ 12 billion Miatas

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Miata is about 13 feet long

Earth's circumference is ~25,000 miles
$\Rightarrow$ 10 million Miatas placed end-to-end

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12 Gigatons C ≈ 12 billion Miatas

Miata is about 13 feet long

Earth's circumference is ~25,000 miles
⇒ 10 million Miatas placed end-to-end

12 Gigatons C is equivalent to a series of Miatas, placed end-to-end, ***encircling the Earth 1,200 times !***

Modern CO_2 Record

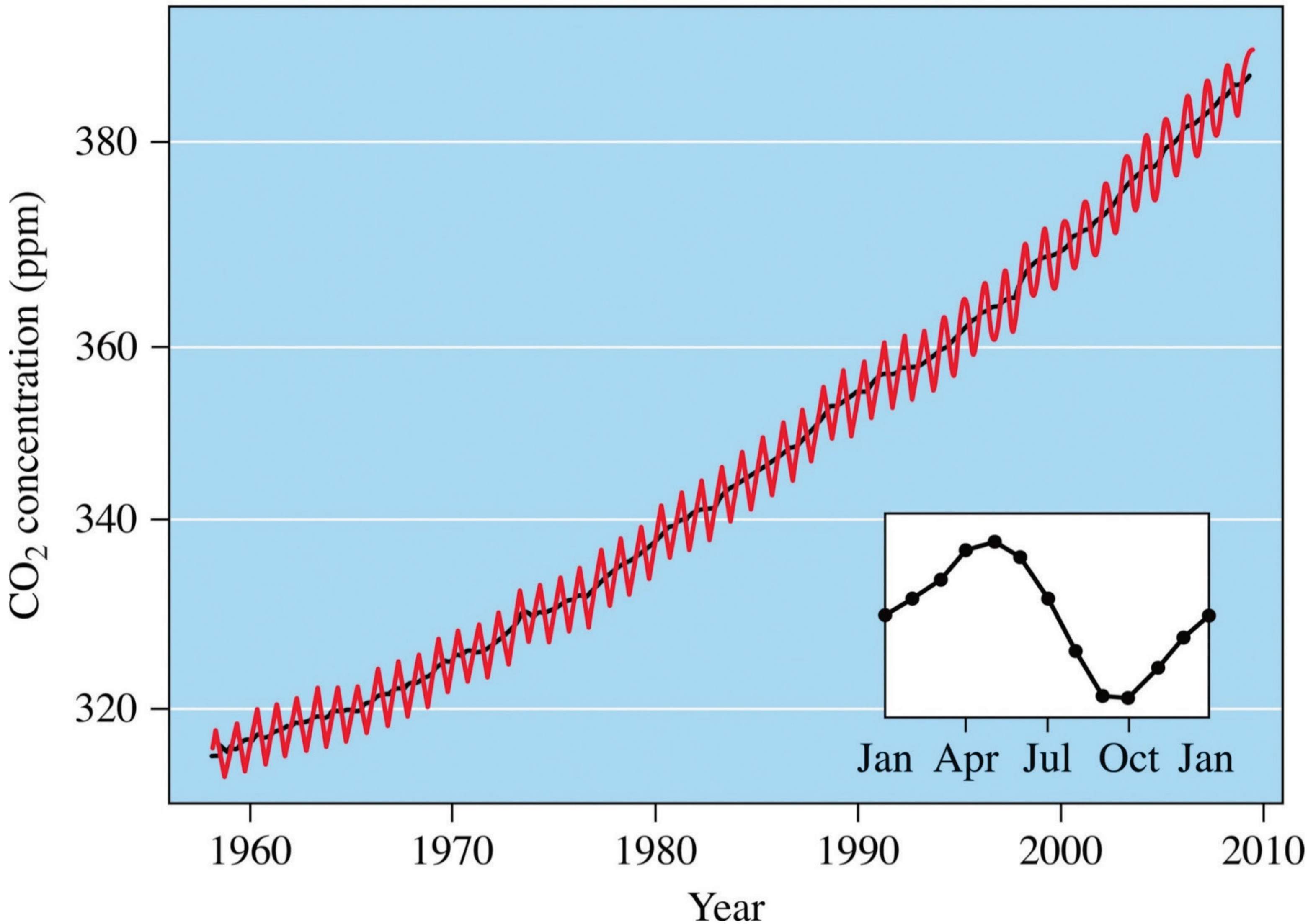
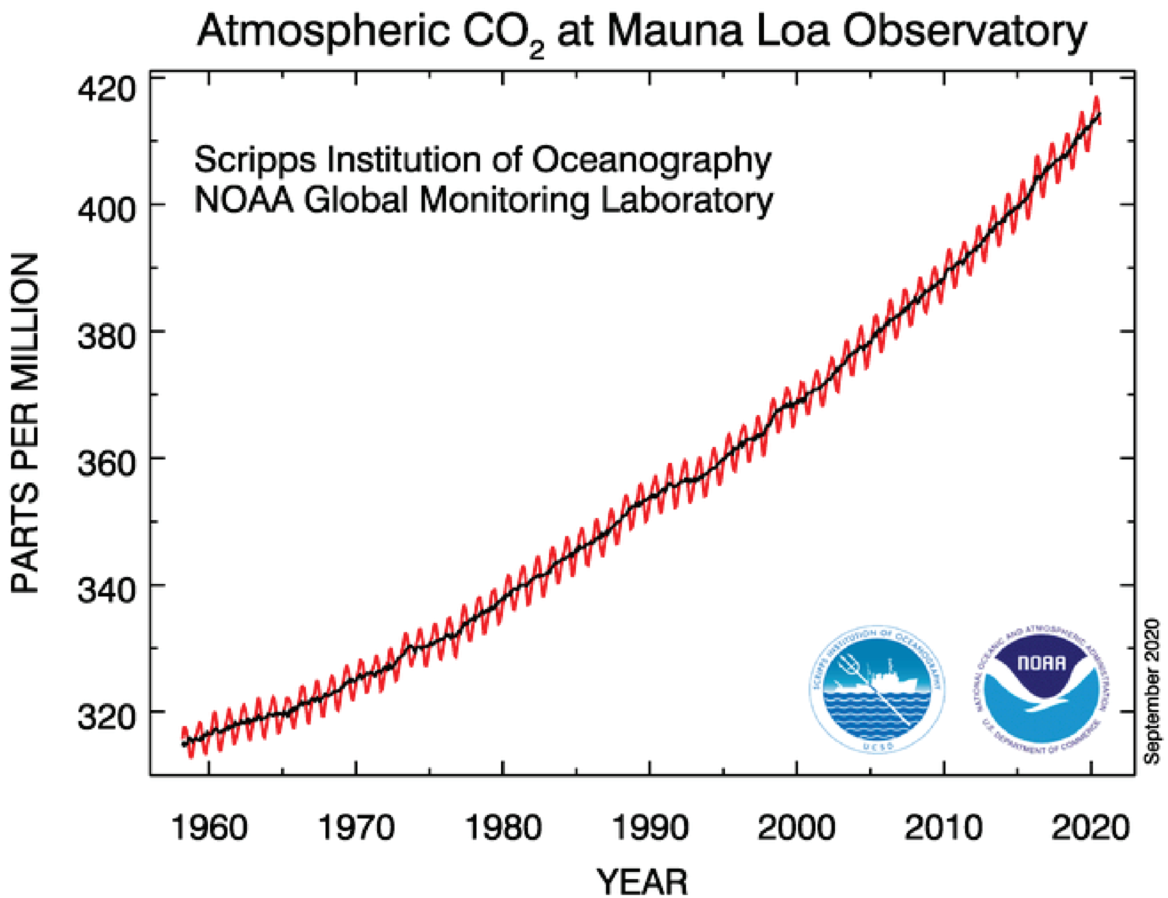


Figure 3.3, Chemistry in Context

Modern CO_2 Record

CO_2 at MLO on 15 Sept 2020: 411.84 parts per million (ppm)
CO_2 at MLO on 14 Sept 2019: 408.12 parts per million (ppm)

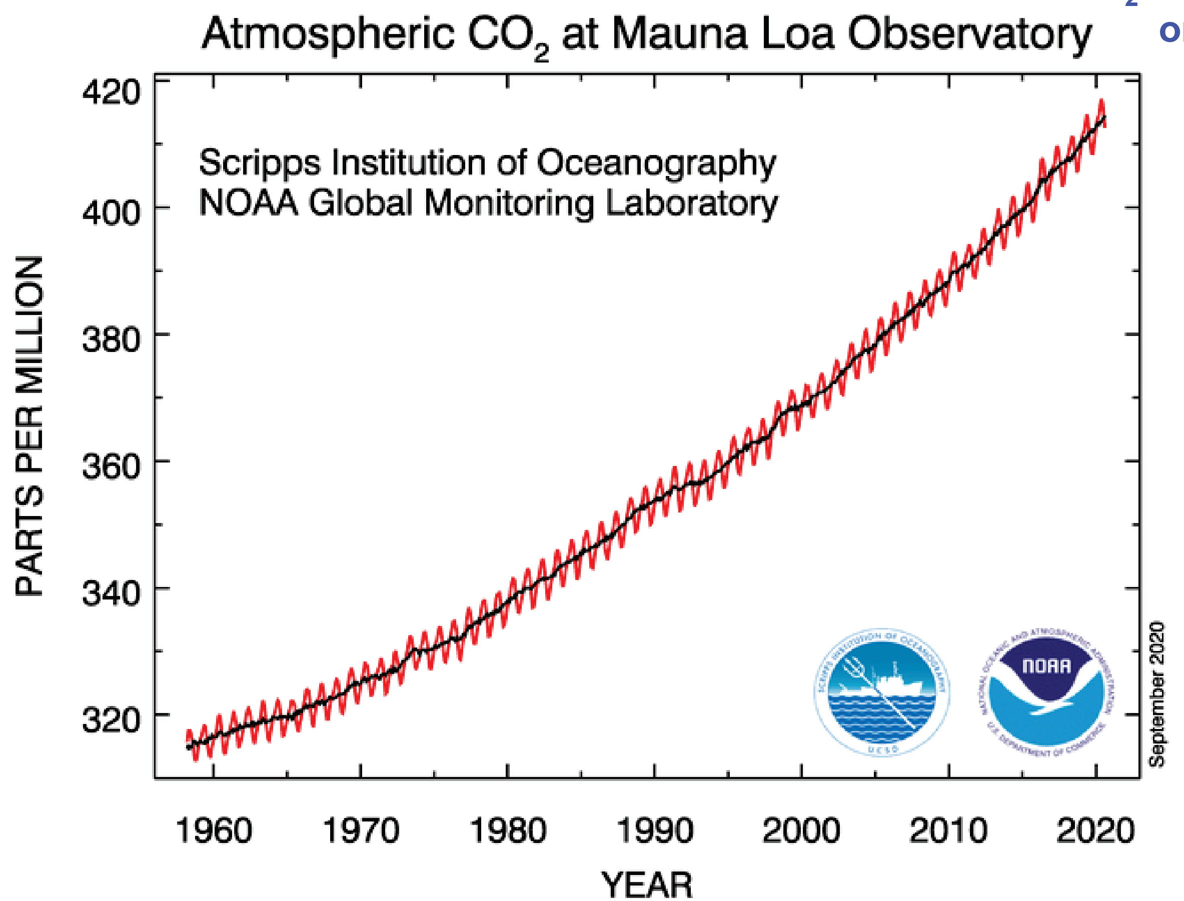


Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
https://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_data_mlo.png
See also https://www.co2.earth/daily-co2

Modern CO_2 Record

CO_2 at MLO on 15 Sept 2020: 411.84 parts per million (ppm)
CO_2 at MLO on 14 Sept 2019: 408.12 parts per million (ppm)

ΔCO_2 = 3.71 ppm per year
or 0.91 % per year



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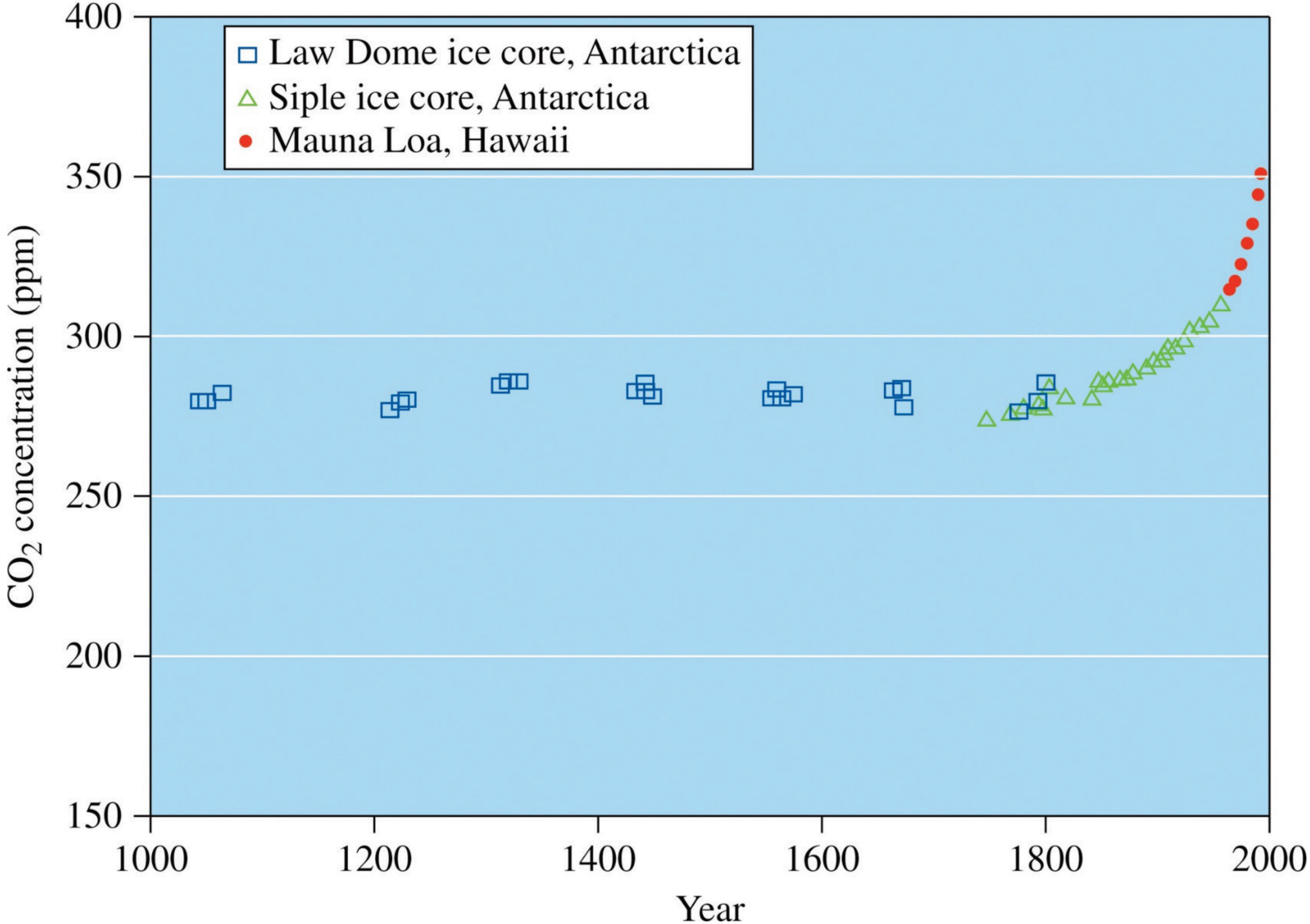


Figure 3.5, *Chemistry in Context, 7th Edition*

Release of CO_2 due to Combustion of Fossil Fuels is Endemic in the Global Economy

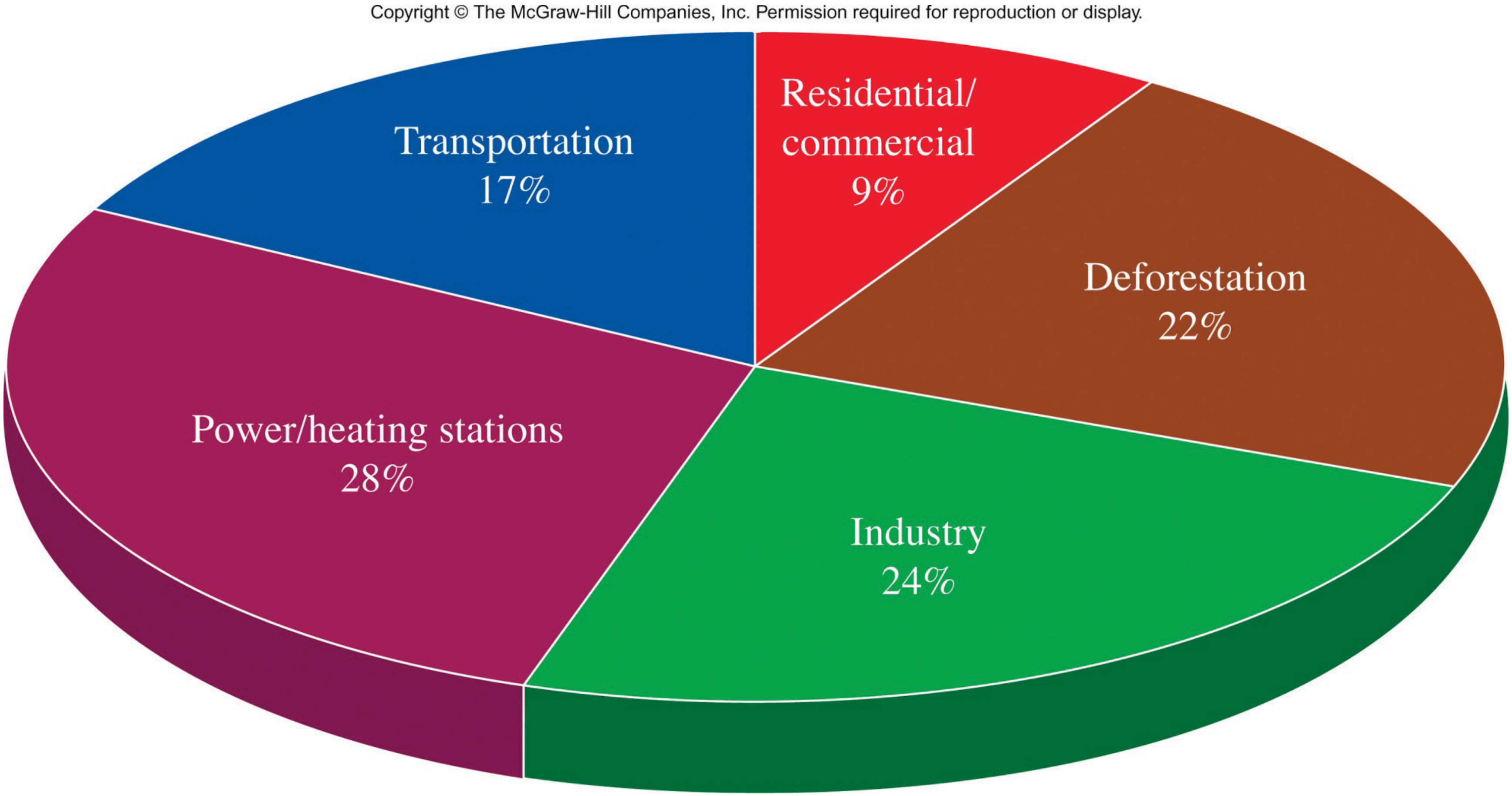


Figure 3.21, *Chemistry in Context, 7th Edition*

Modern CO_2 Record

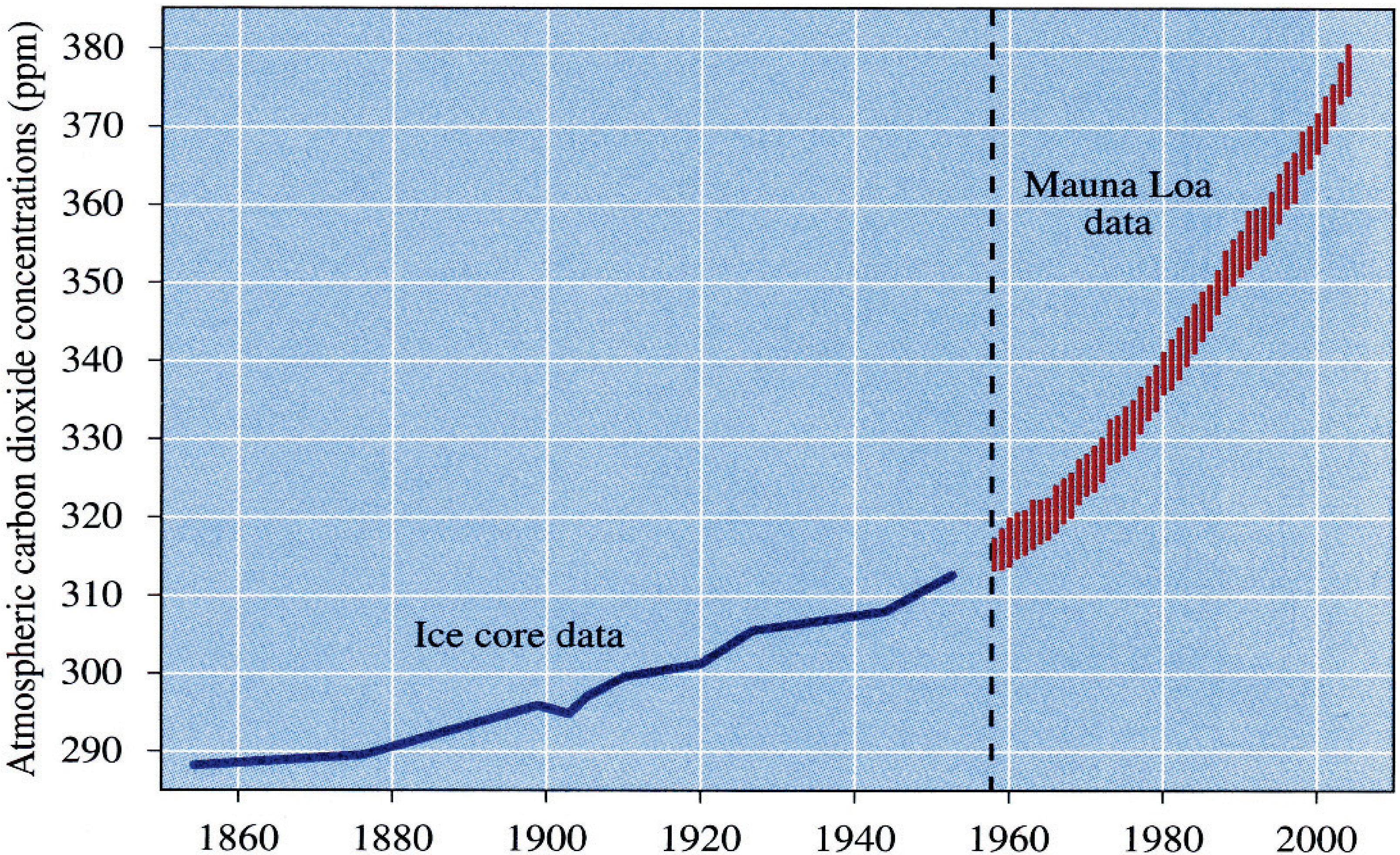
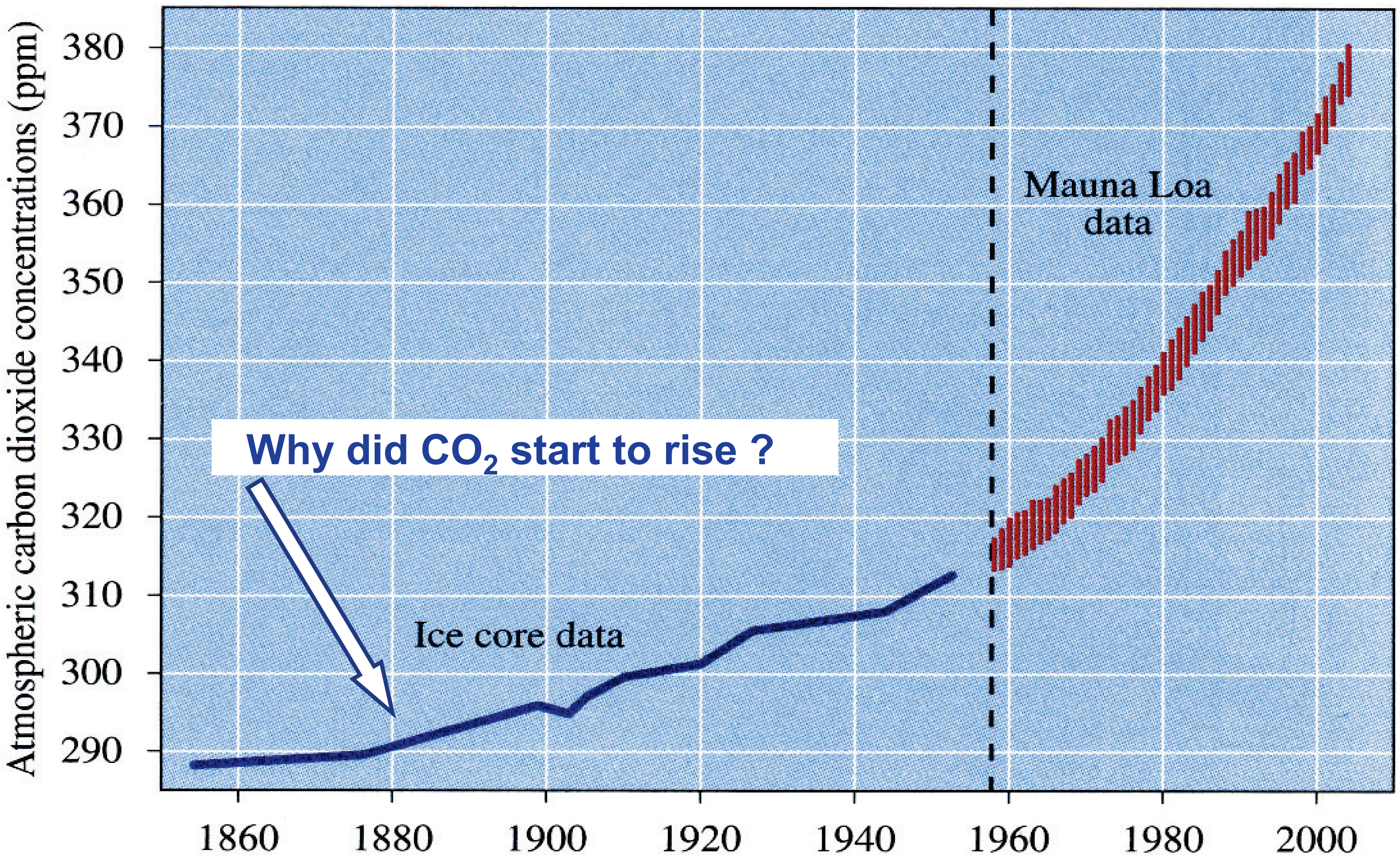


Figure 3.5, *Chemistry in Context, 6th Edition*

Modern CO_2 Record



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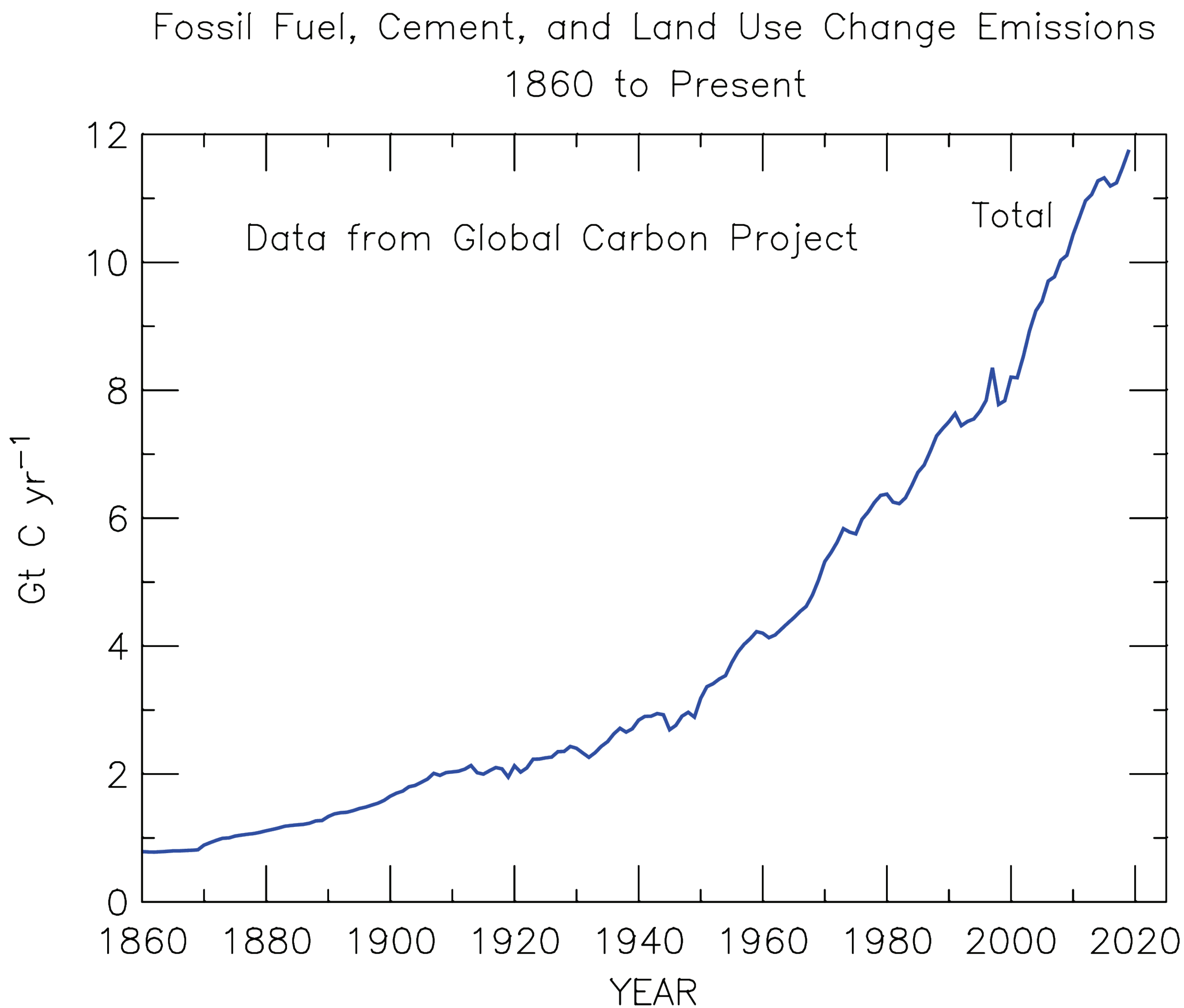
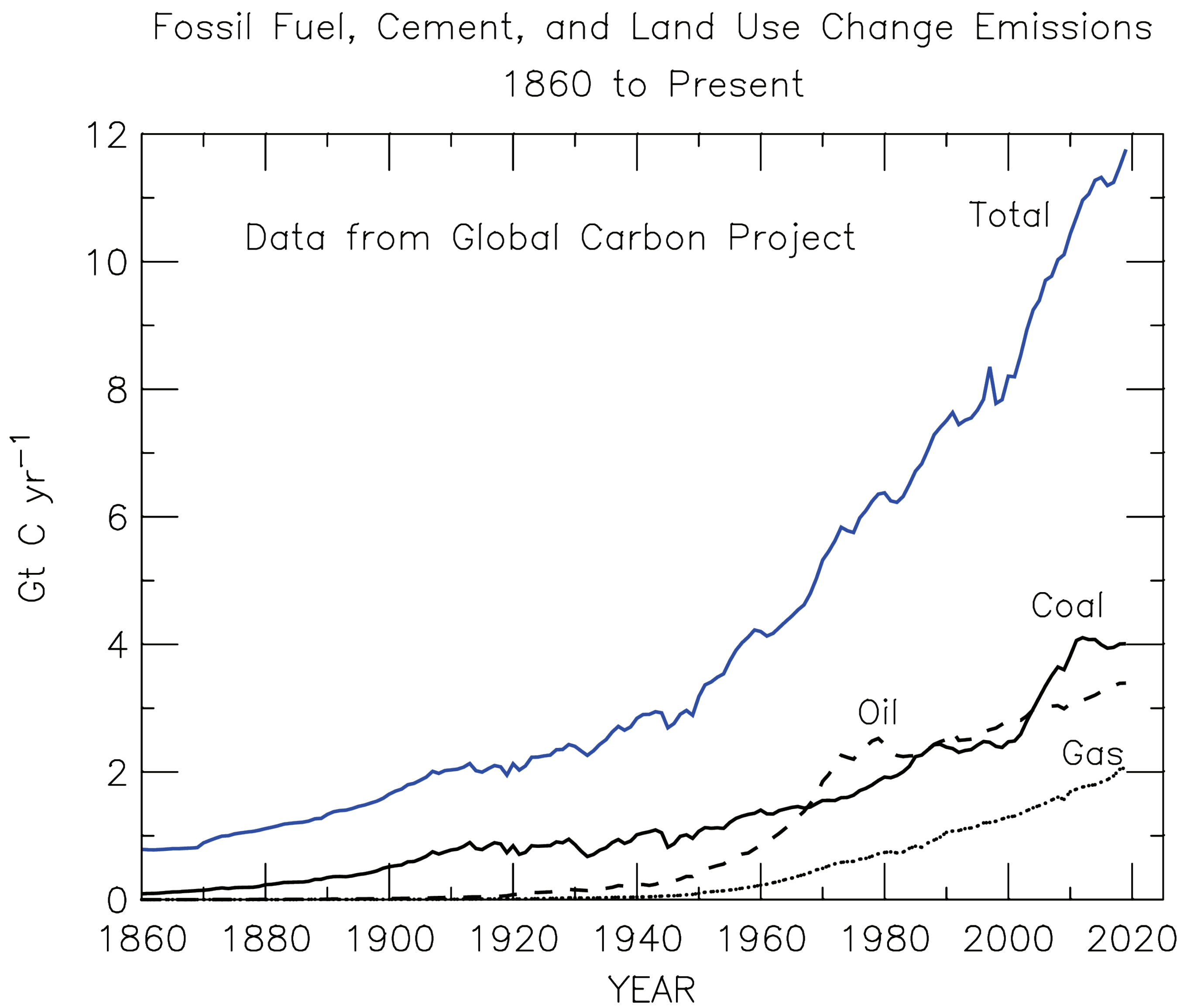
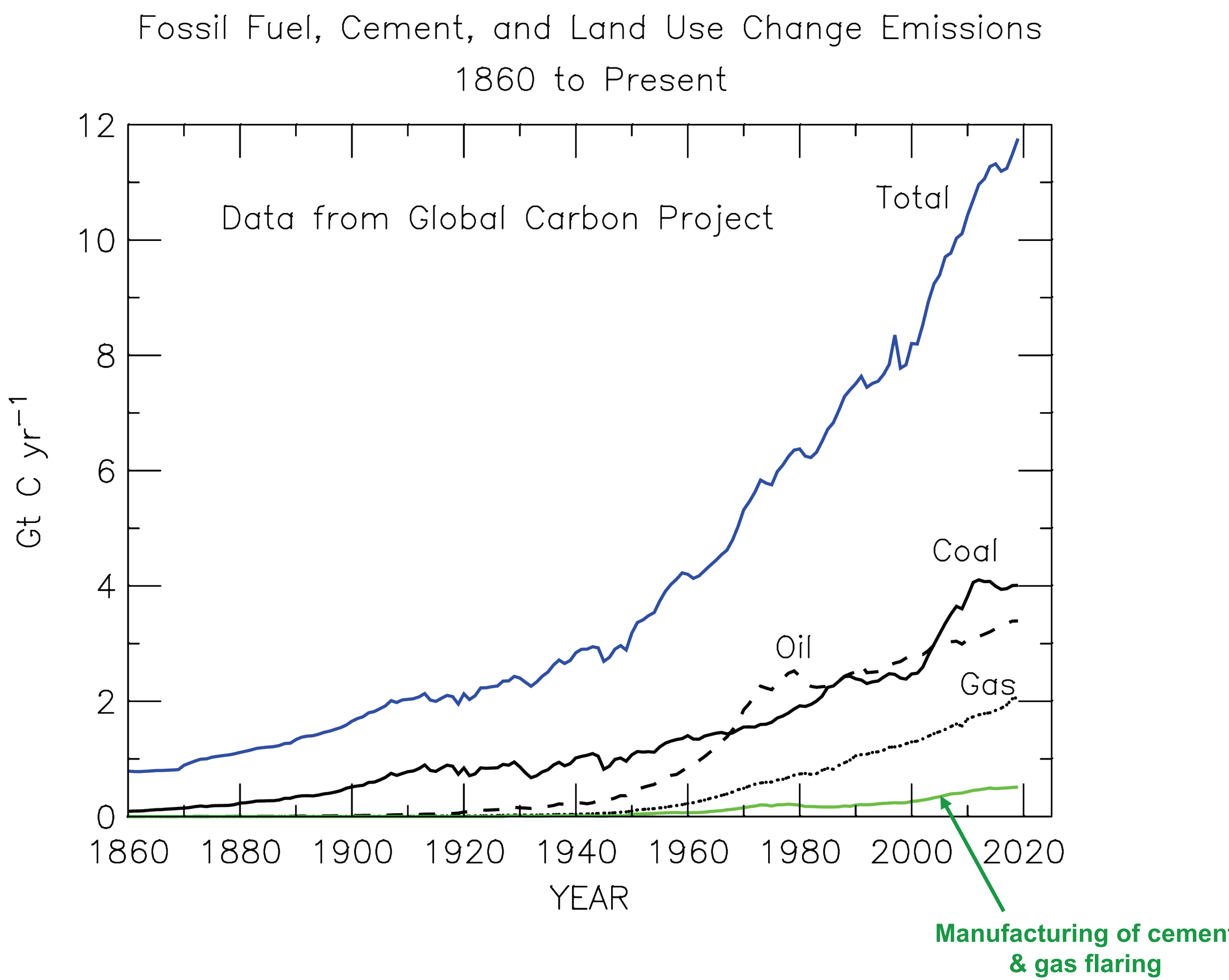

Fossil Fuel, Cement, and Land Use Change Emissions
1860 to Present
Data from Global Carbon Project
Total
Gt C yr^{-1}
0
2
4
6
8
10
12
1860
1880
1900
1920
1940
1960
1980
2000
2020
YEAR



Fossil Fuel, Cement, and Land Use Change Emissions
1860 to Present
Data from Global Carbon Project
Total
Coal
Oil
Gas
Gt C yr^{-1}
0
2
4
6
8
10
12
1860
1880
1900
1920
1940
1960
1980
2000
2020
YEAR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1860 to Present
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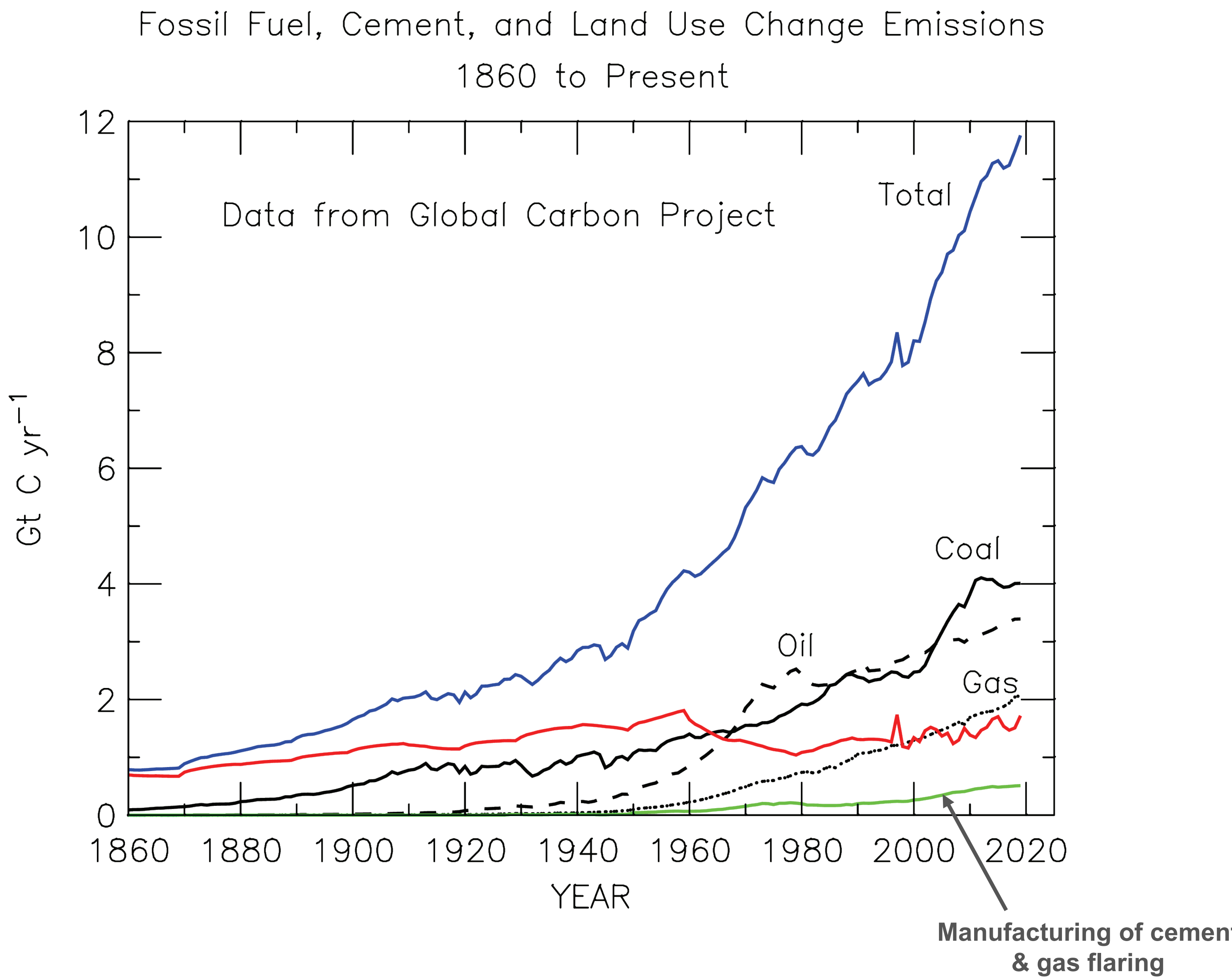
Total
Coal
Oil
Gas
Gt C yr^{-1}
YEAR
0
2
4
6
8
10
12
1860
1880
1900
1920
1940
1960
1980
2000
2020
Manufacturing of cement
& gas flaring



Fossil Fuel, Cement, and Land Use Change Emissions
1860 to Present
Data from Global Carbon Project
Total
Coal
Oil
Gas
Gt C yr⁻¹
YEAR
0
2
4
6
8
10
12
1860
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1900
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1940
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Manufacturing of cement
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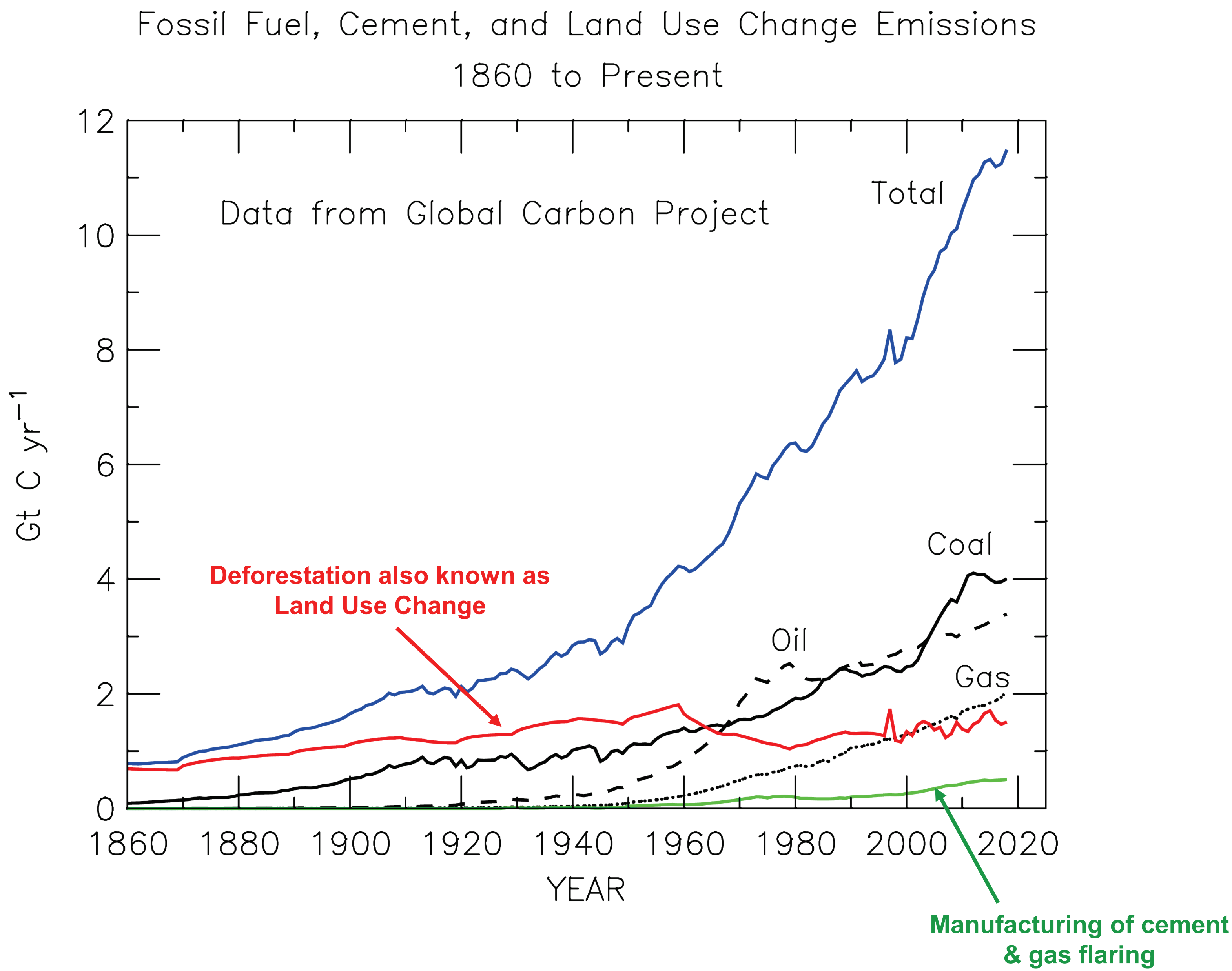

Fossil Fuel, Cement, and Land Use Change Emissions
1860 to Present
Data from Global Carbon Project
Total
Coal
Oil
Gas
Deforestation also known as
Land Use Change
Manufacturing of cement
& gas flaring
Gt C yr^{-1}
YEAR
0
2
4
6
8
10
12
1860
1880
1900
1920
1940
1960
1980
2000
2020

Modern CO_2 Record

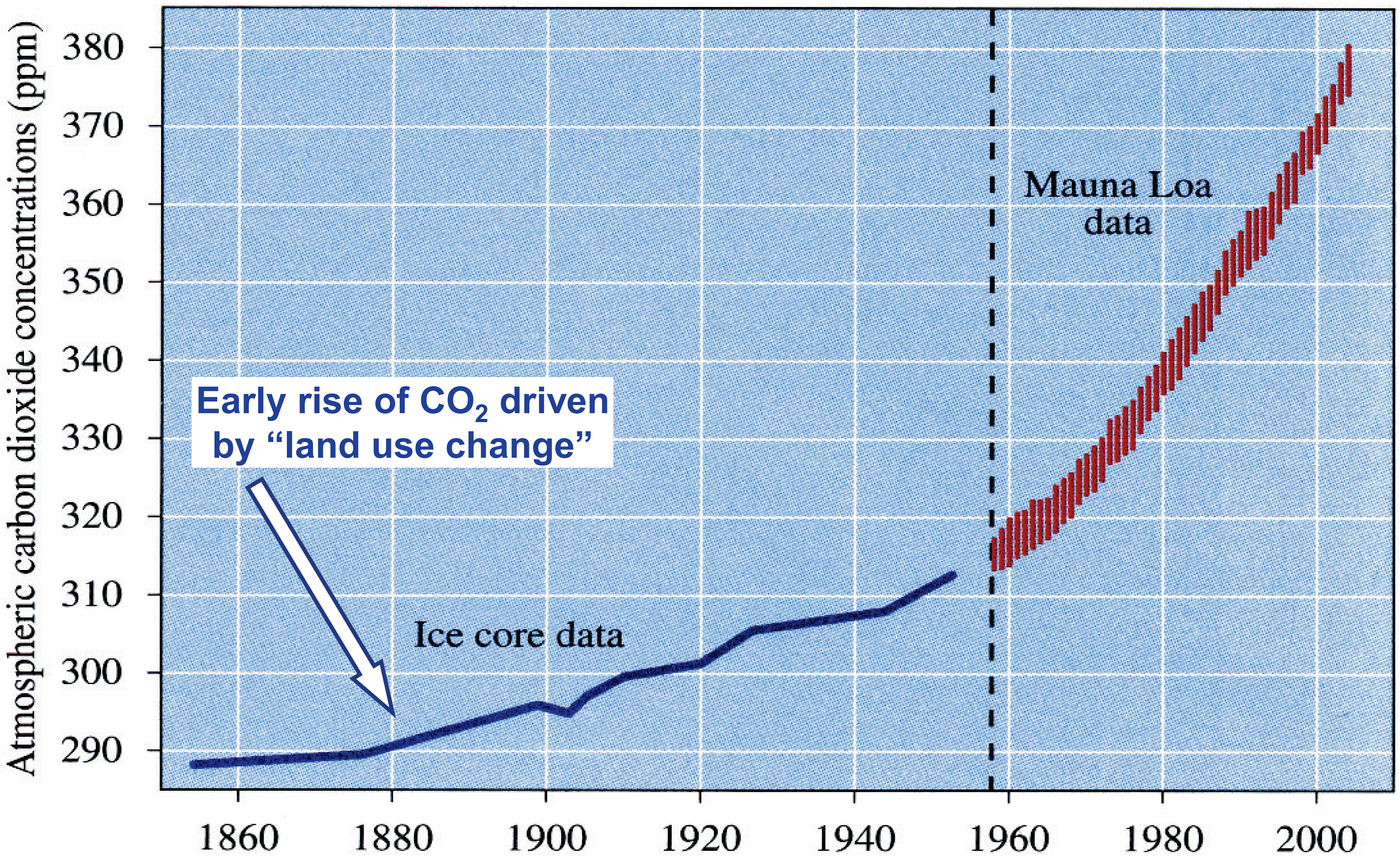


Figure 3.5, *Chemistry in Context, 6th Edition*

Modern CO_2 Record

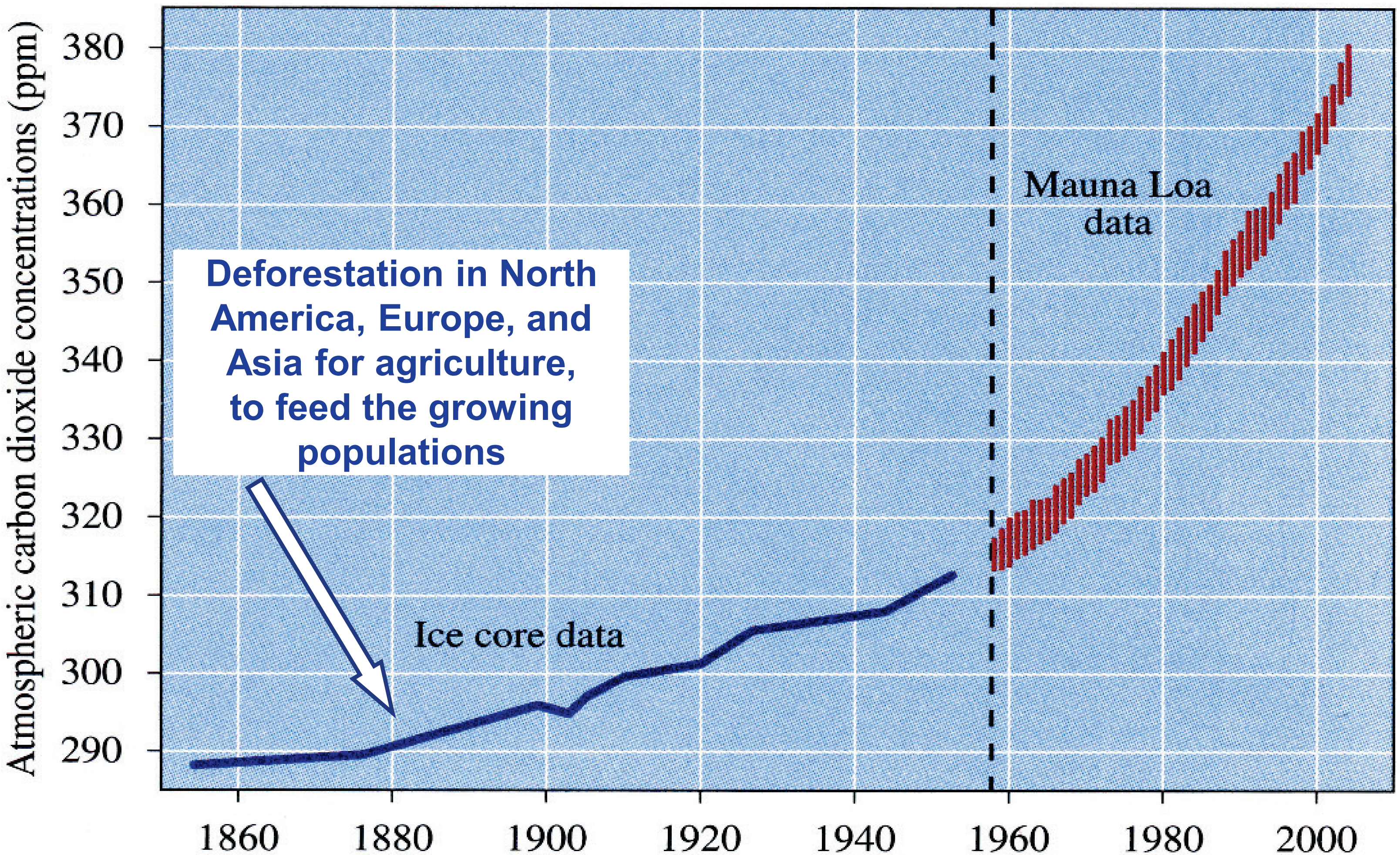


Figure 3.5, *Chemistry in Context, 6th Edition*

Human “Fingerprints” on Atmospheric CO_2

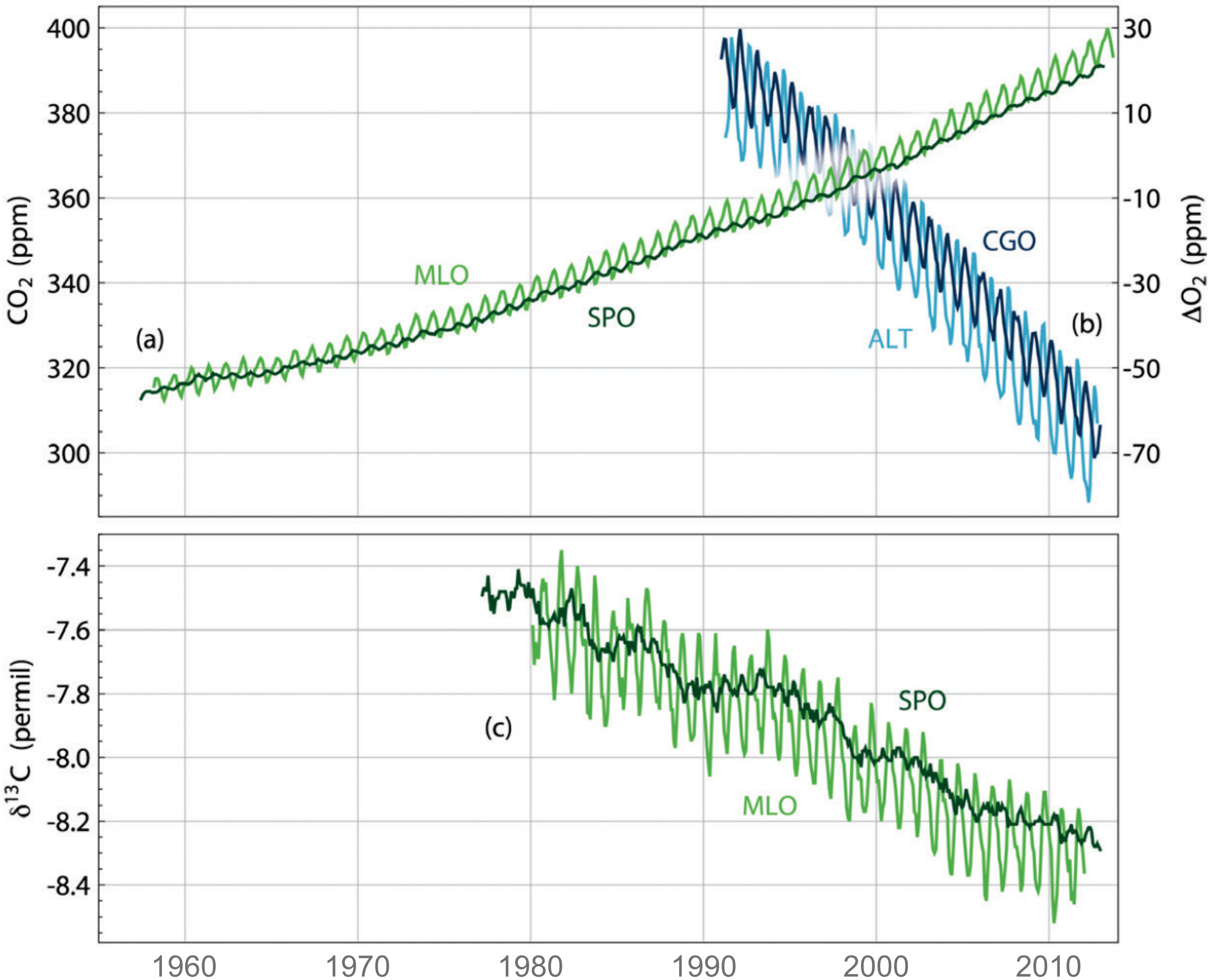
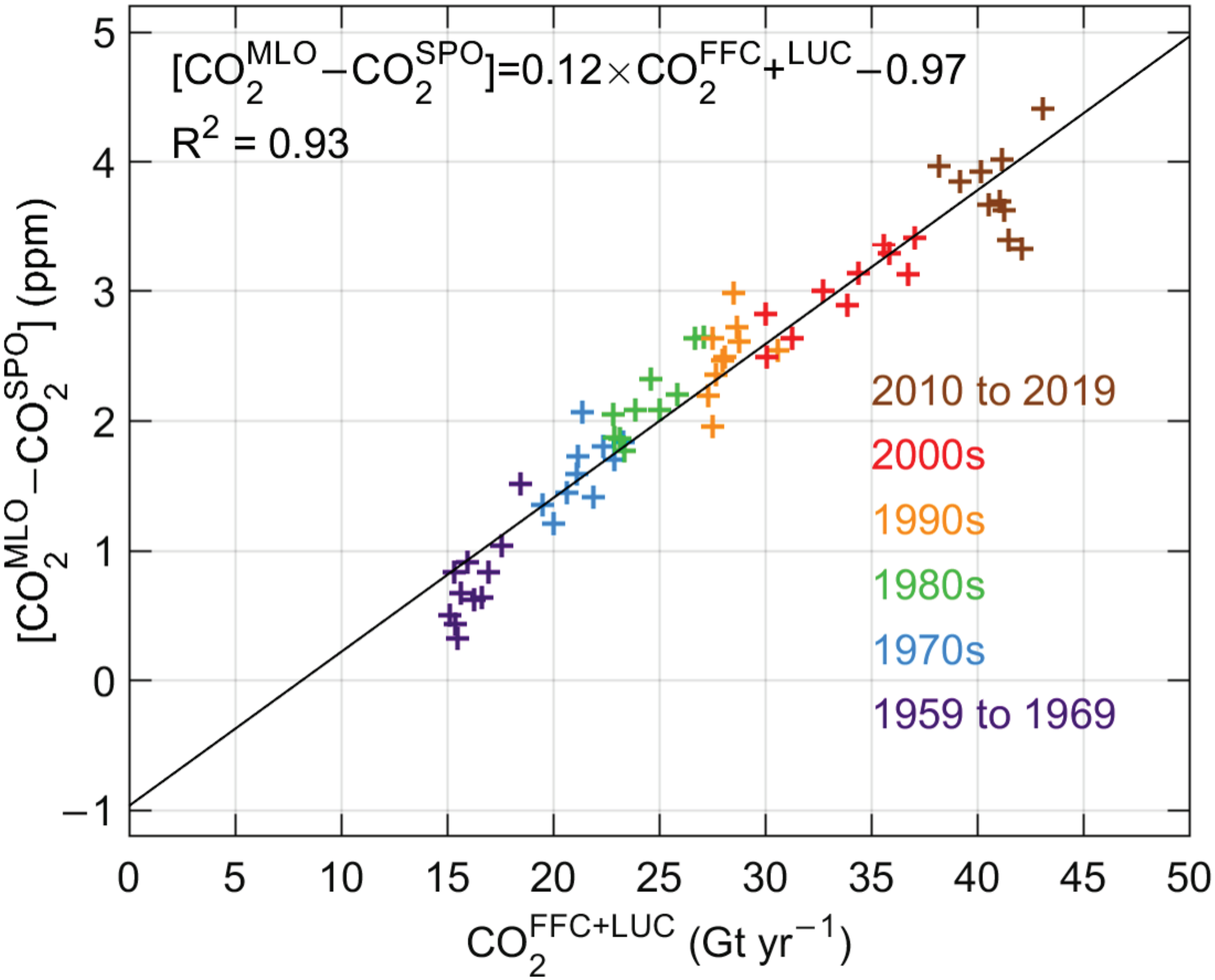


Figure 3.4 Atmospheric concentrations observed at representative stations of (a) carbon dioxide from Mauna Loa (MLO) Northern Hemisphere and South Pole (SPO) Southern Hemisphere; (b) Oxygen from Alert (ALT) Canada, 82°N, and Cape Grim (CGO), Australia, 41°S; (c) $^{13}C/^{12}C$ from Mauna Loa (MLO) and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

Fig 3.4, Houghton

Human "Fingerprints" on Atmospheric CO_2



MLO: Mauna Loa Observatory
SPO: South Pole Observatory
FFC: Fossil Fuel Combustion
LUC: Land Use Change (Deforestation)

Fig 1.8 updated, *Paris Beacon of Hope*

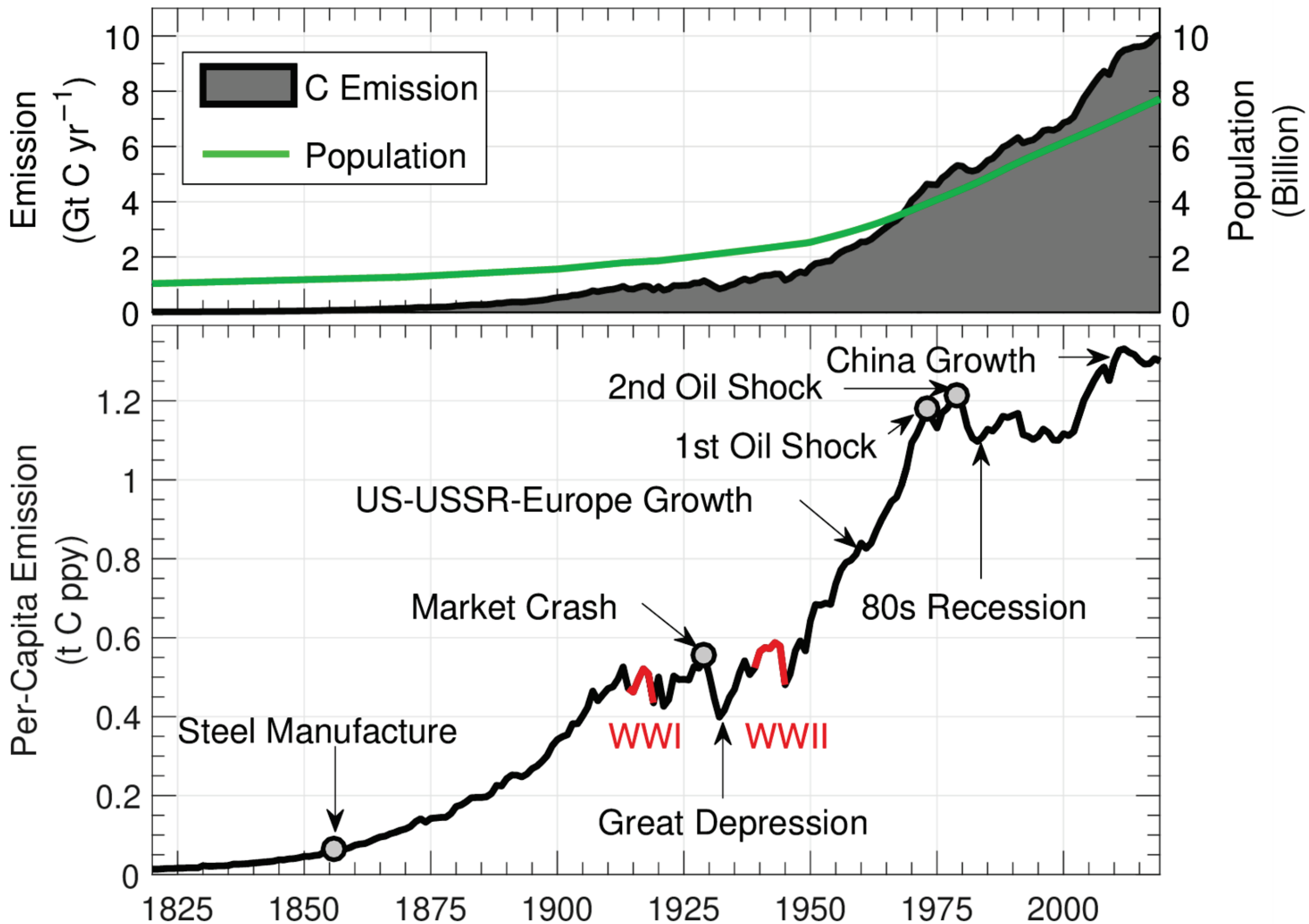
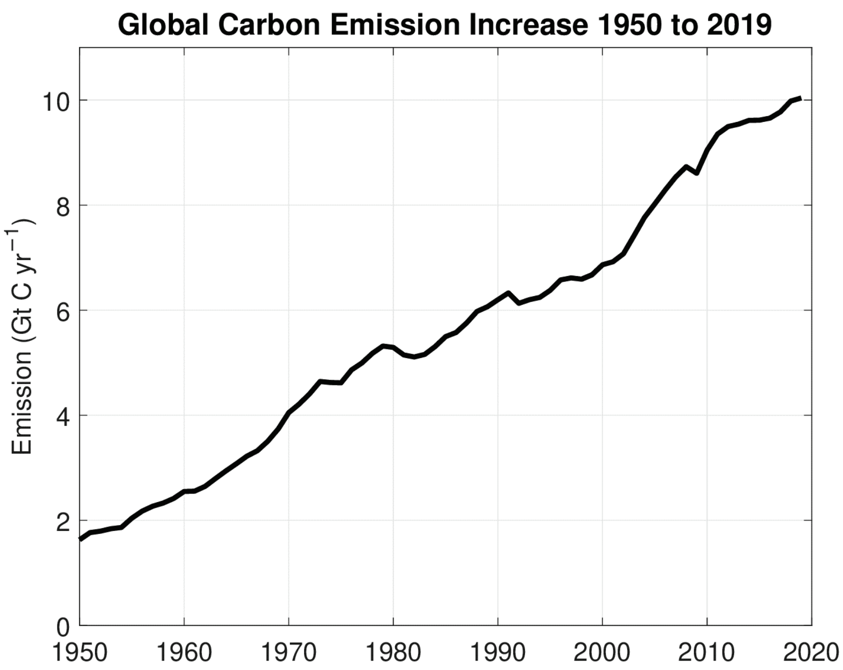


Figure courtesy Walt Tribett

After Fig 3.1 *Paris Beacon of Hope*

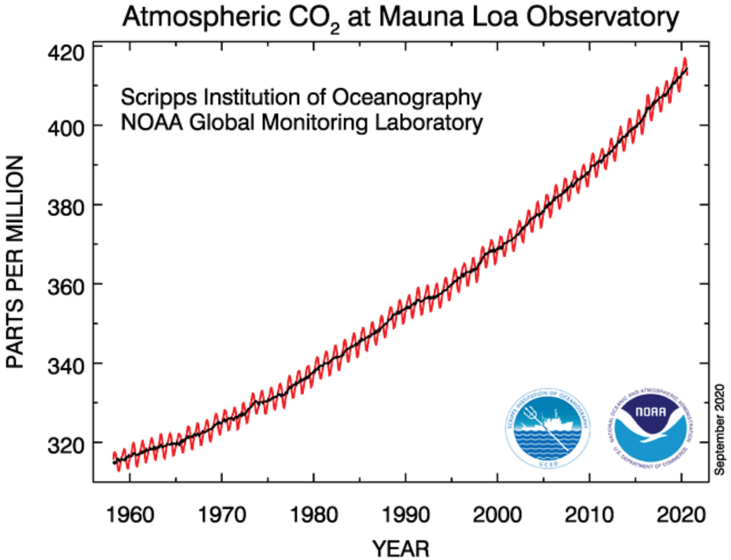
Fossil Fuel Emissions



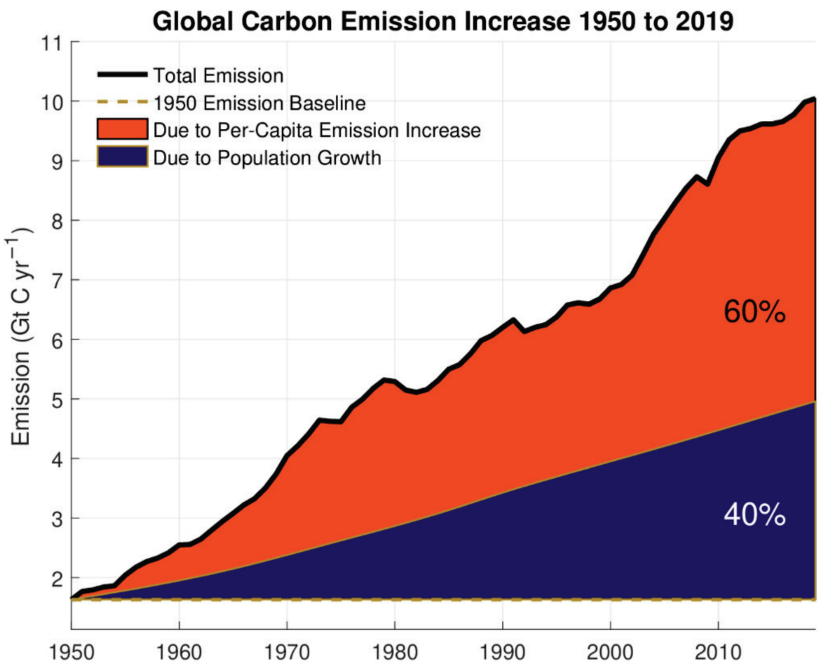
For Problem Set 2 (boo dat), you will relate the mass of cumulative emissions of CO_2 (units of Gt C; see slide 14) to the rise in atmospheric CO_2 (also in units of Gt C)

For today:

What are the primary social factors driving factors responsible for the rise in carbon emissions?

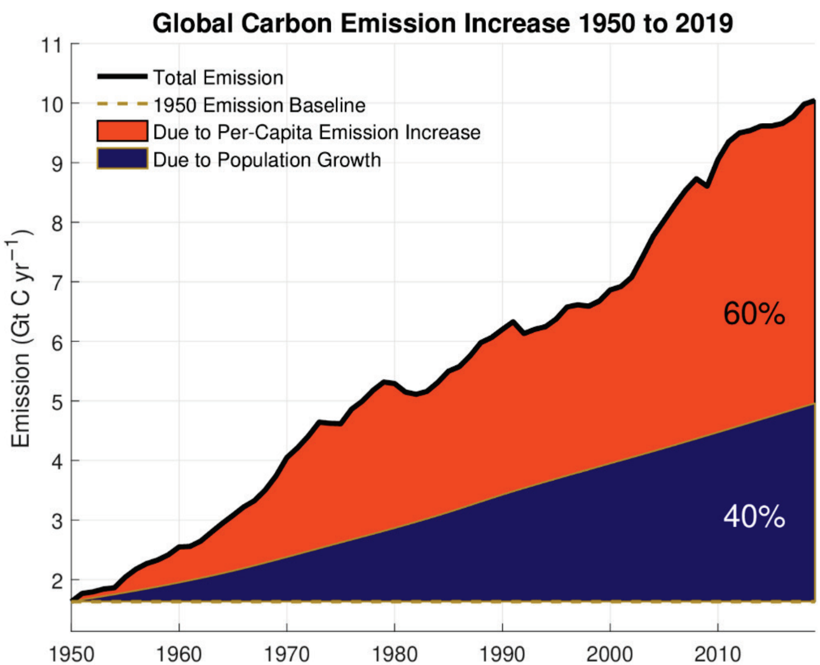


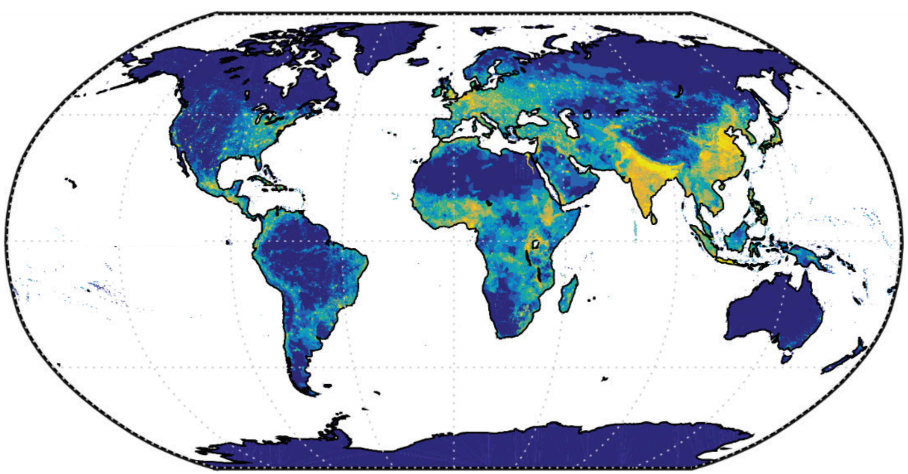
Fossil Fuel Emissions



Population increase & **per-capita rise** both contribute, with *per-capita rise being slightly more important*

Fossil Fuel Emissions





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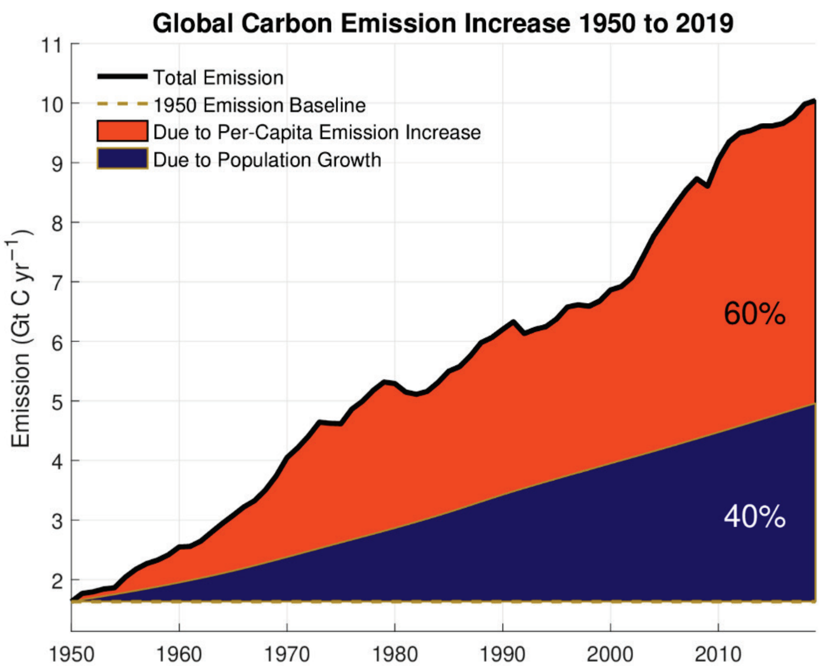

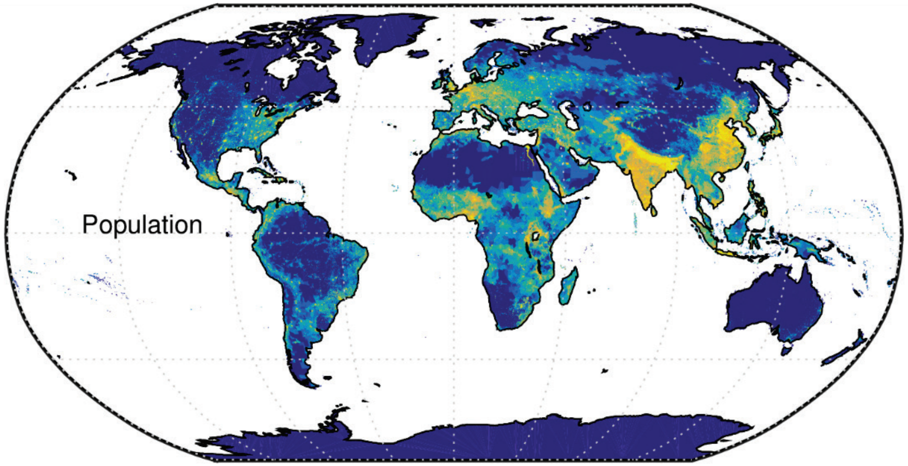

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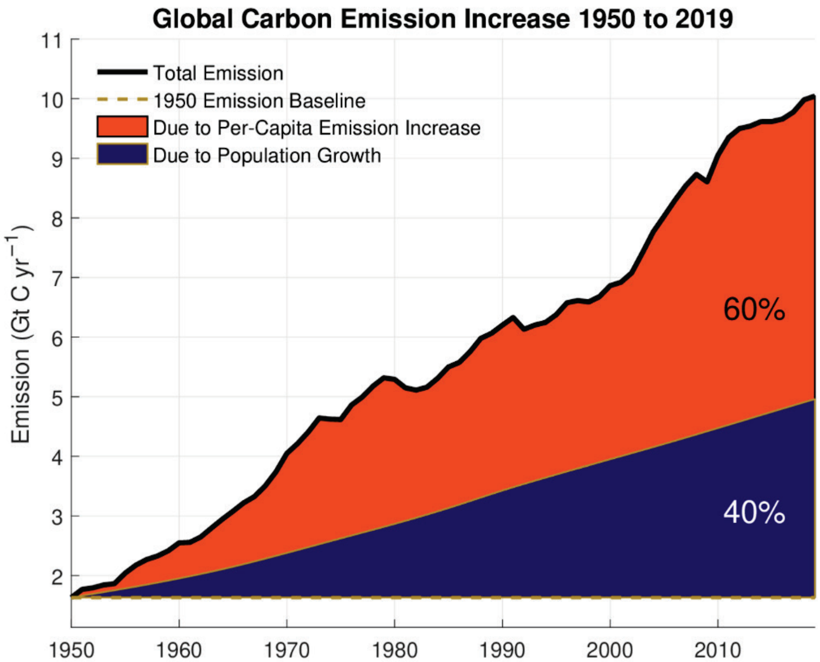

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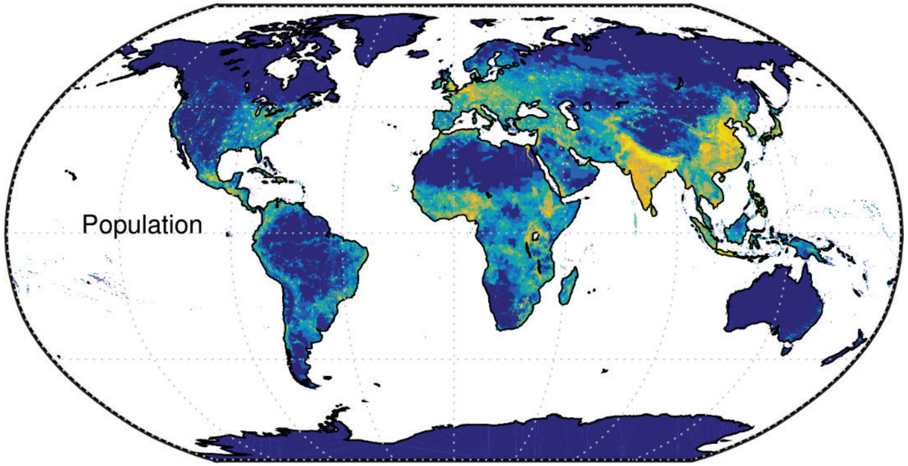
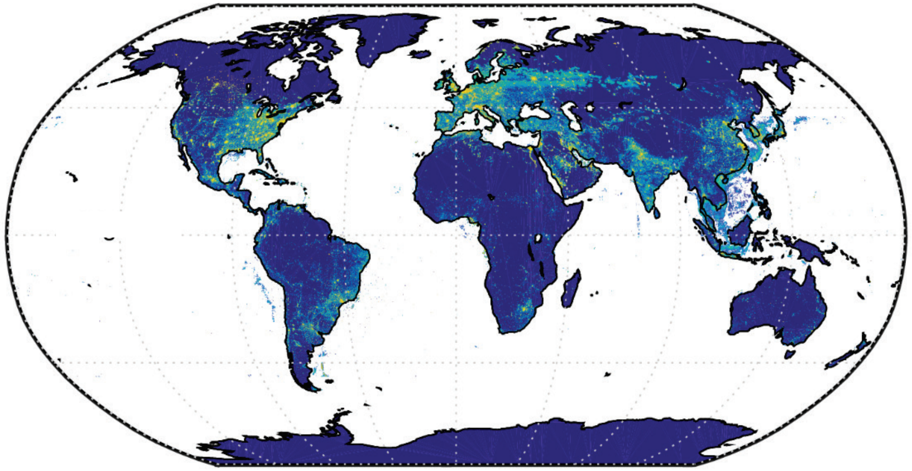
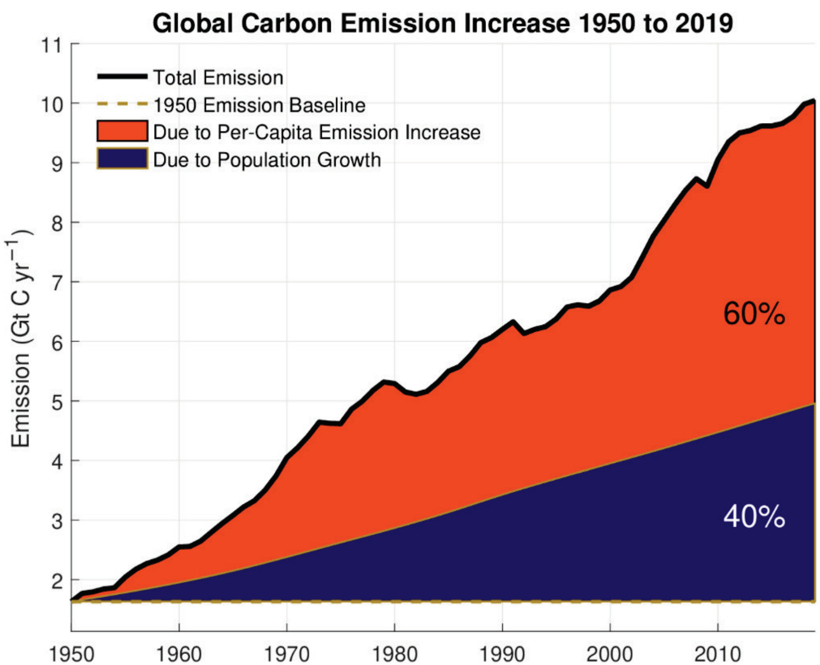




Fossil Fuel Emissions



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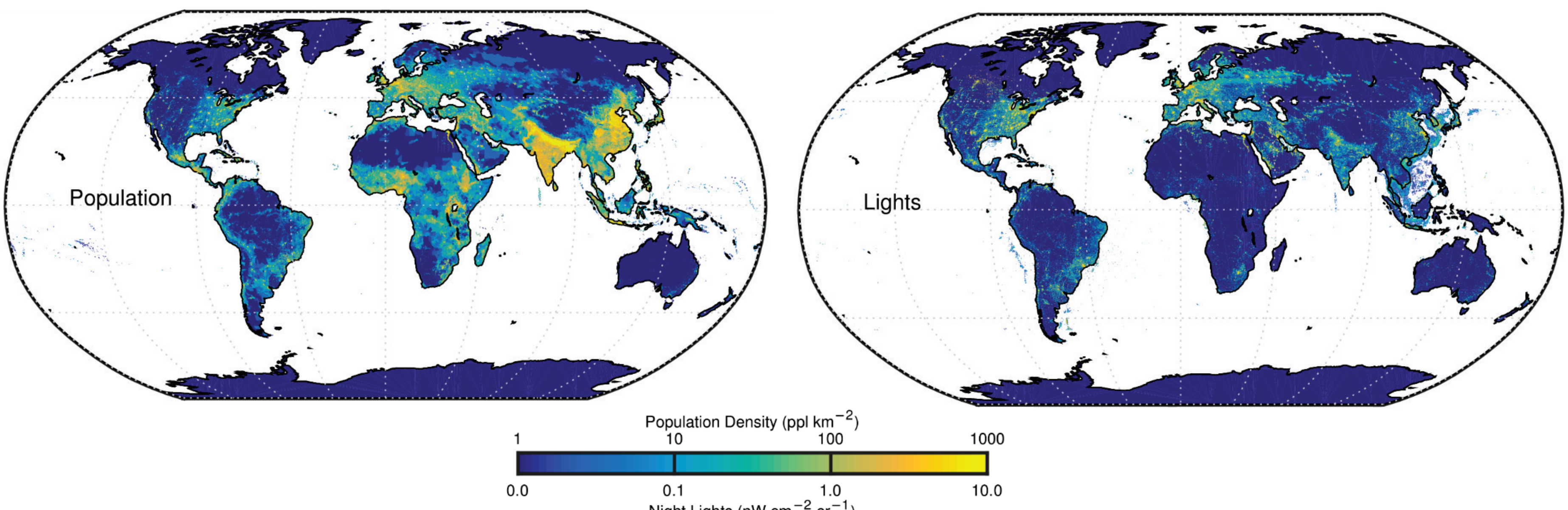
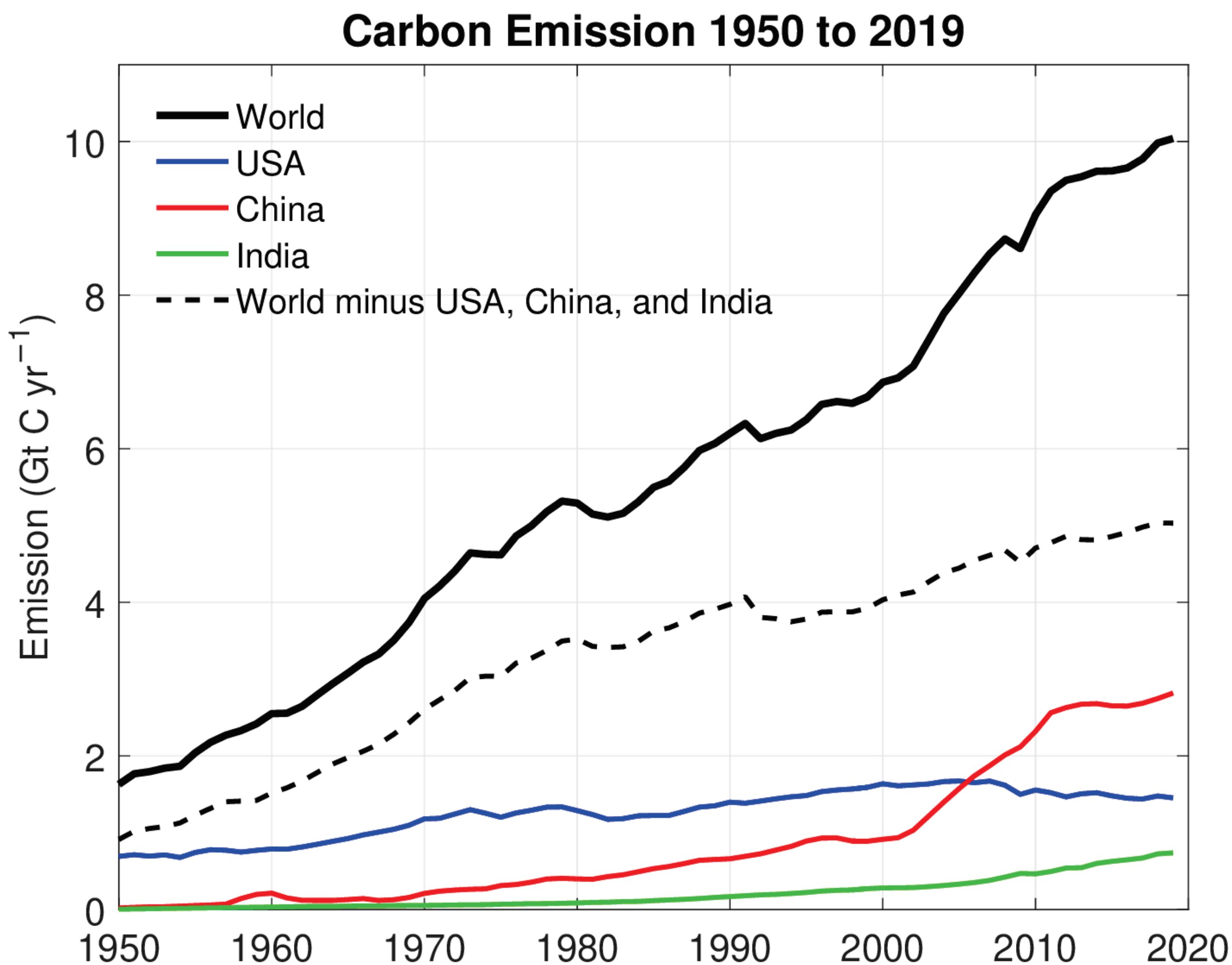
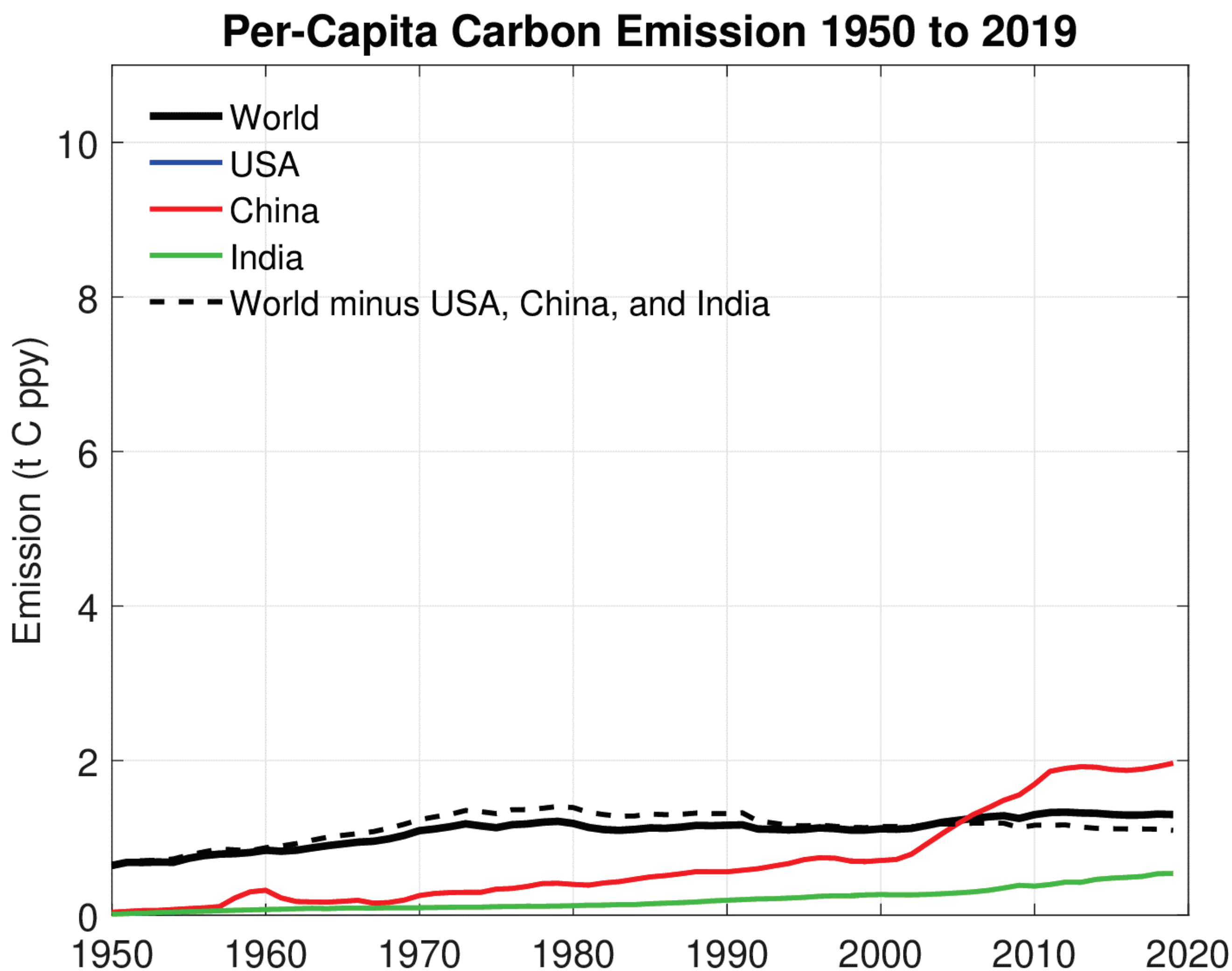
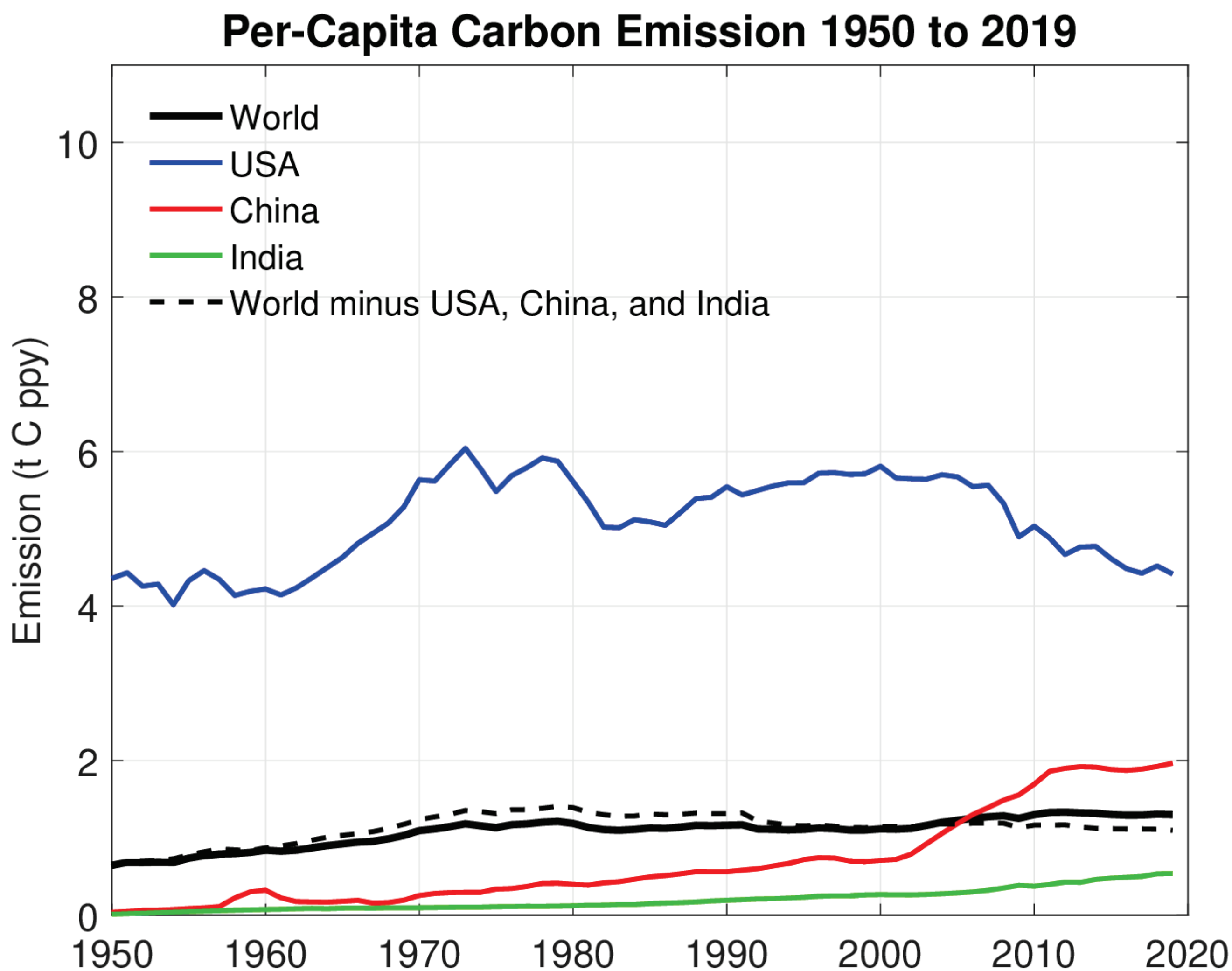




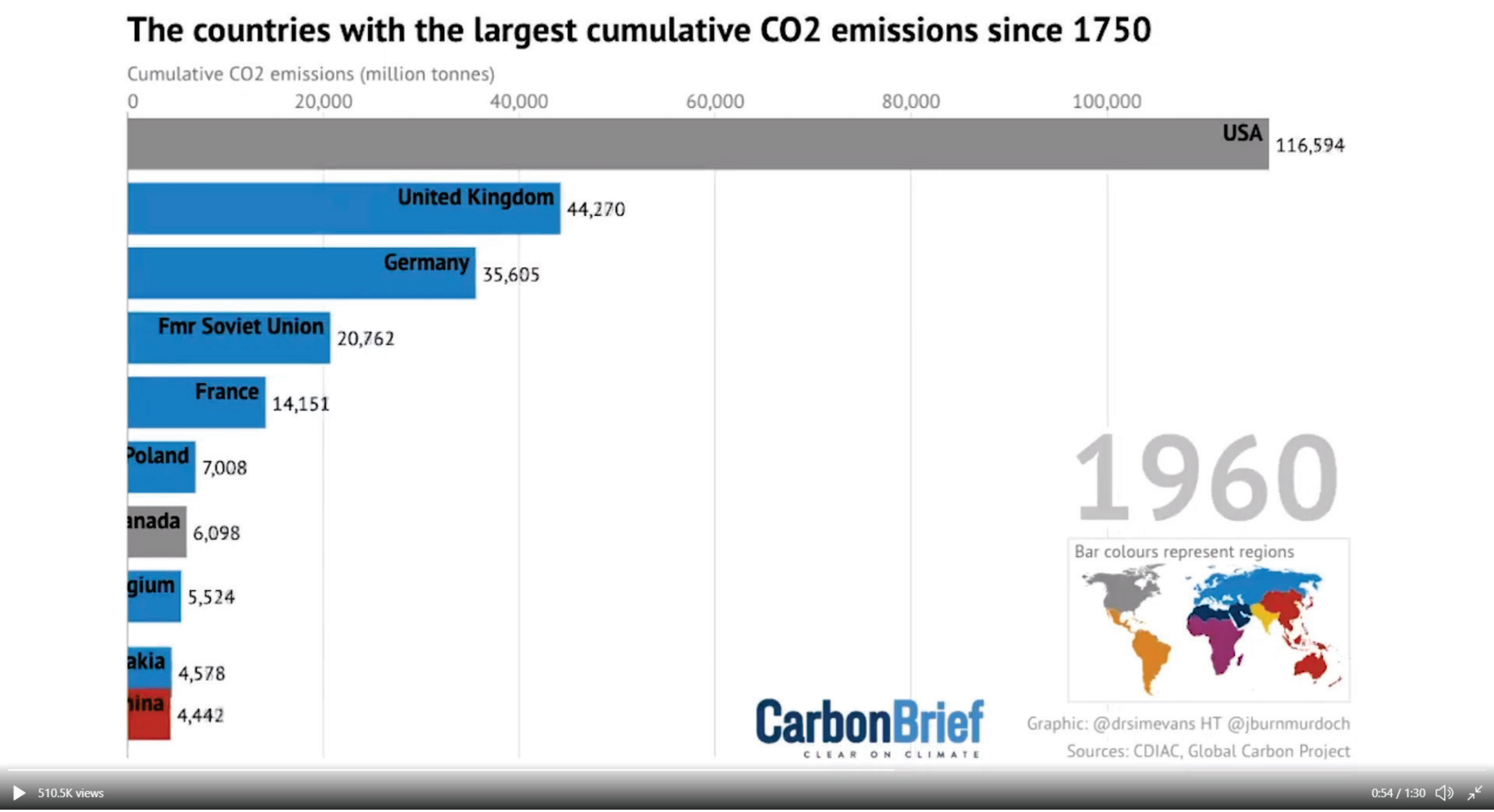
Carbon Emission 1950 to 2019
World
USA
China
India
World minus USA, China, and India
Emission (Gt C yr^{-1})
0
2
4
6
8
10
1950
1960
1970
1980
1990
2000
2010
2020


Per-Capita Carbon Emission 1950 to 2019
World
USA
China
India
World minus USA, China, and India
Emission (t C ppy)
0
2
4
6
8
10
1950
1960
1970
1980
1990
2000
2010
2020



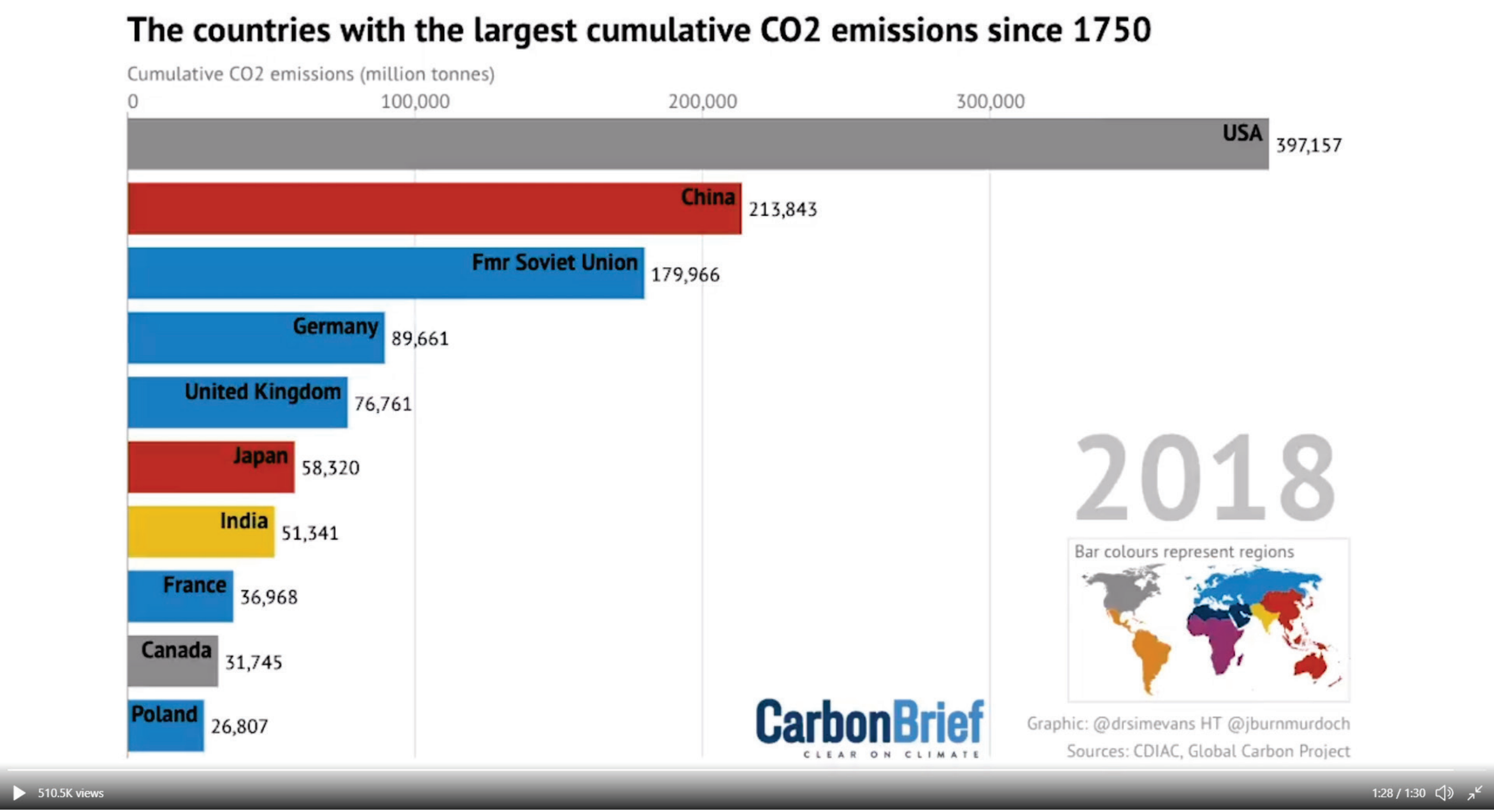
Per-Capita Carbon Emission 1950 to 2019
World
USA
China
India
World minus USA, China, and India
Emission (t C ppy)
0
2
4
6
8
10
1950
1960
1970
1980
1990
2000
2010
2020

Fossil Fuel Emission Animation



https://twitter.com/i/status/1120715988532629506

Fossil Fuel Emission Animation



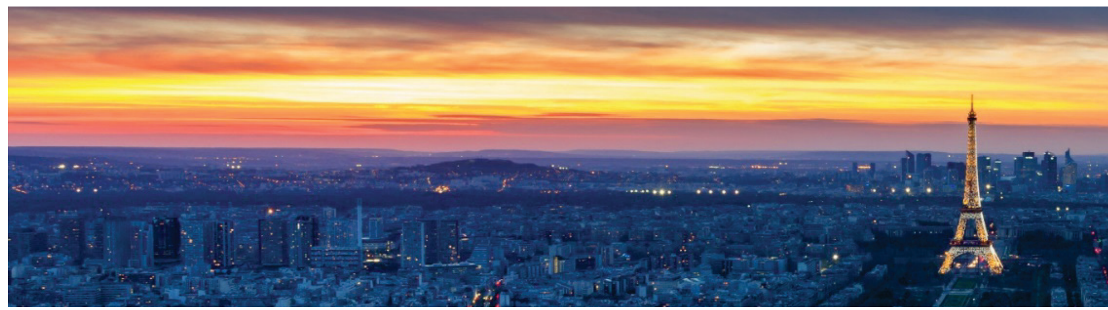
https://twitter.com/i/status/1120715988532629506

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

Global Carbon Cycle

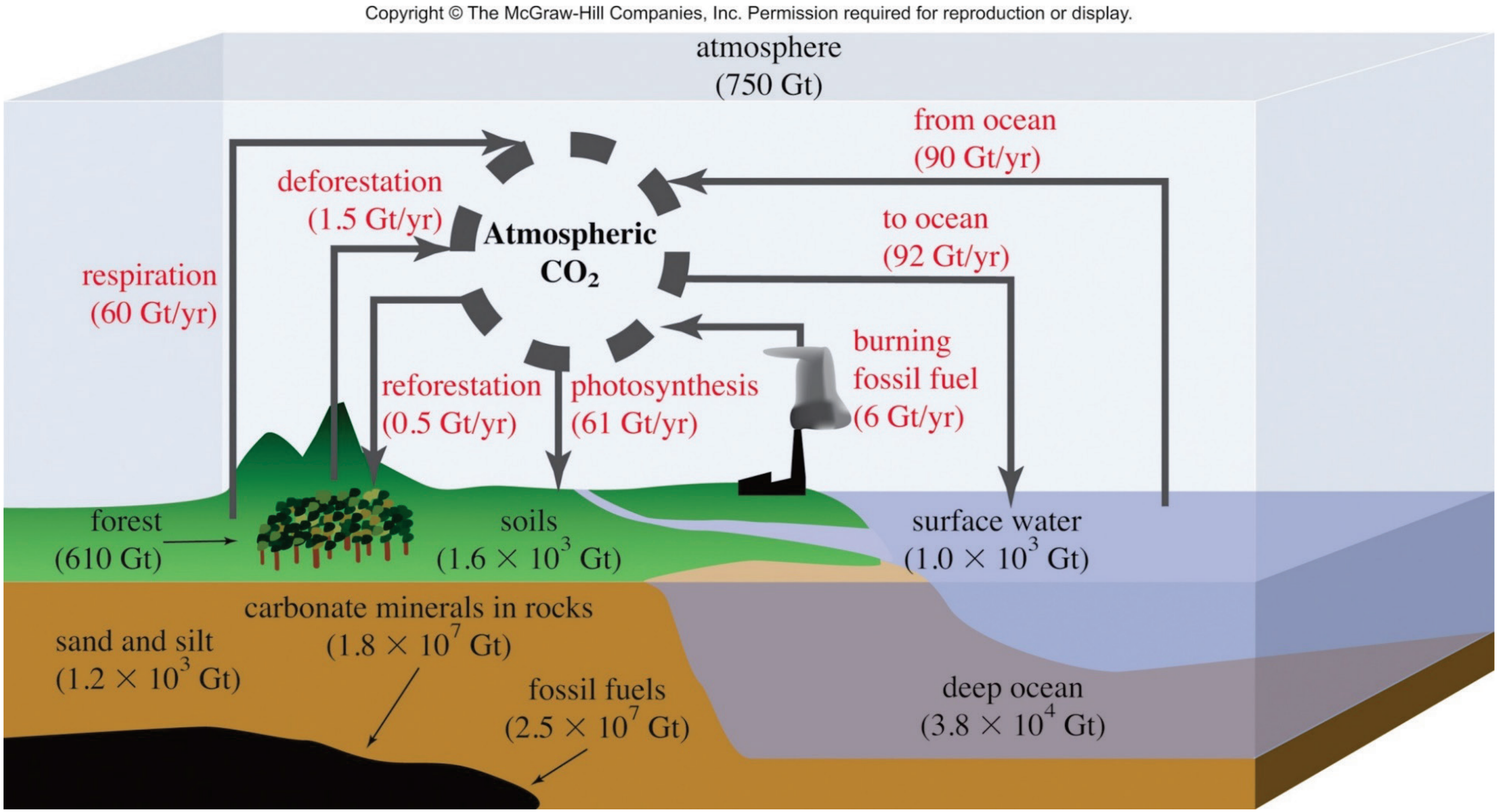


Fig 3.20, Chemistry in Context

Global Carbon Cycle

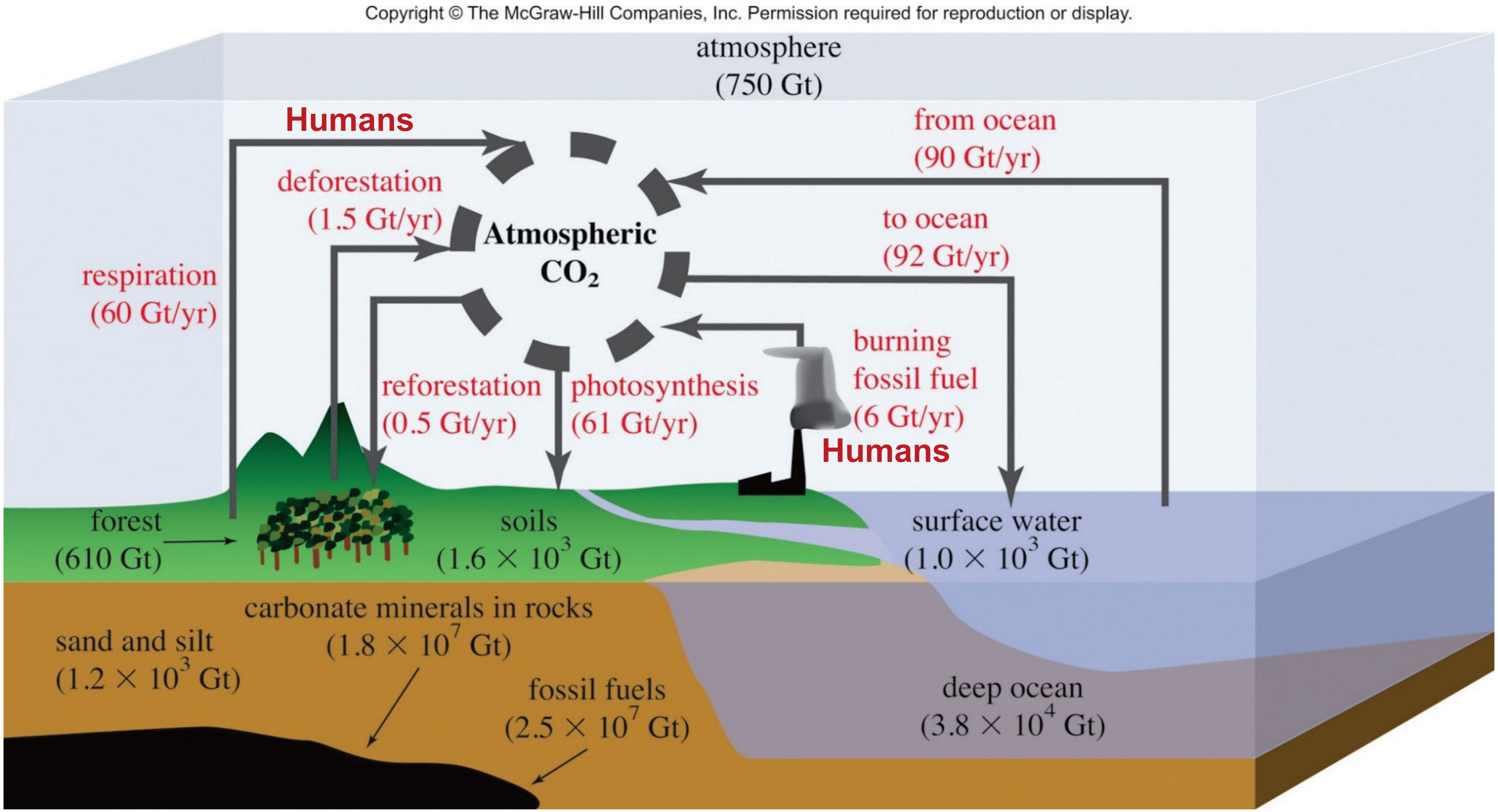


Fig 3.20, Chemistry in Context

CC:

Human Release = 6 Gt per year + 1.5 Gt per year = 7.5 Gt per year

Global Carbon Cycle

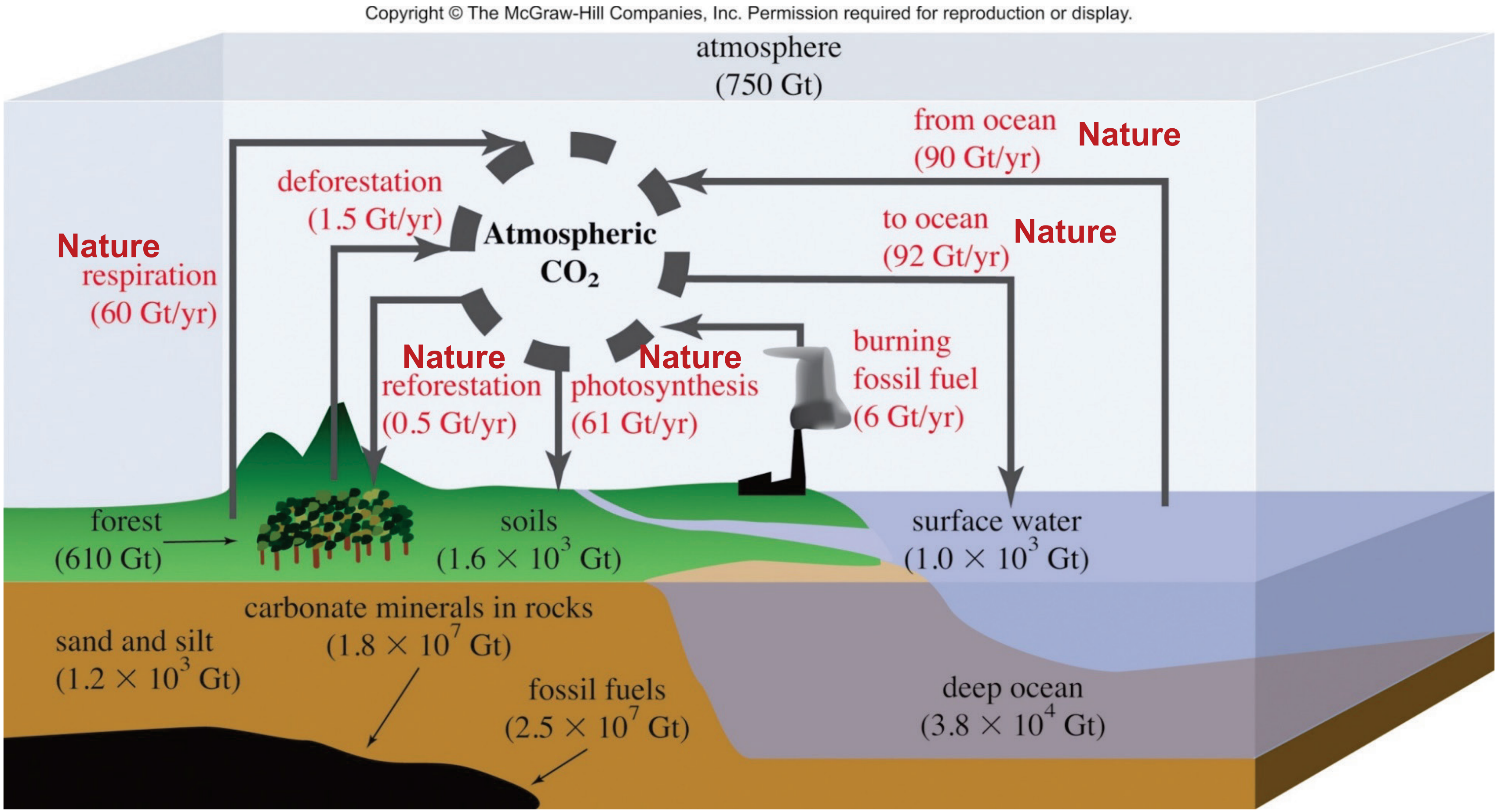


Fig 3.20, Chemistry in Context

CC:

Land Sink = (61 + 0.5) – (60) Gt C / yr = 1.5 Gt C / yr
Ocean Sink = 92 – 90 Gt C / yr = 2 Gt C / yr

Global Carbon Cycle

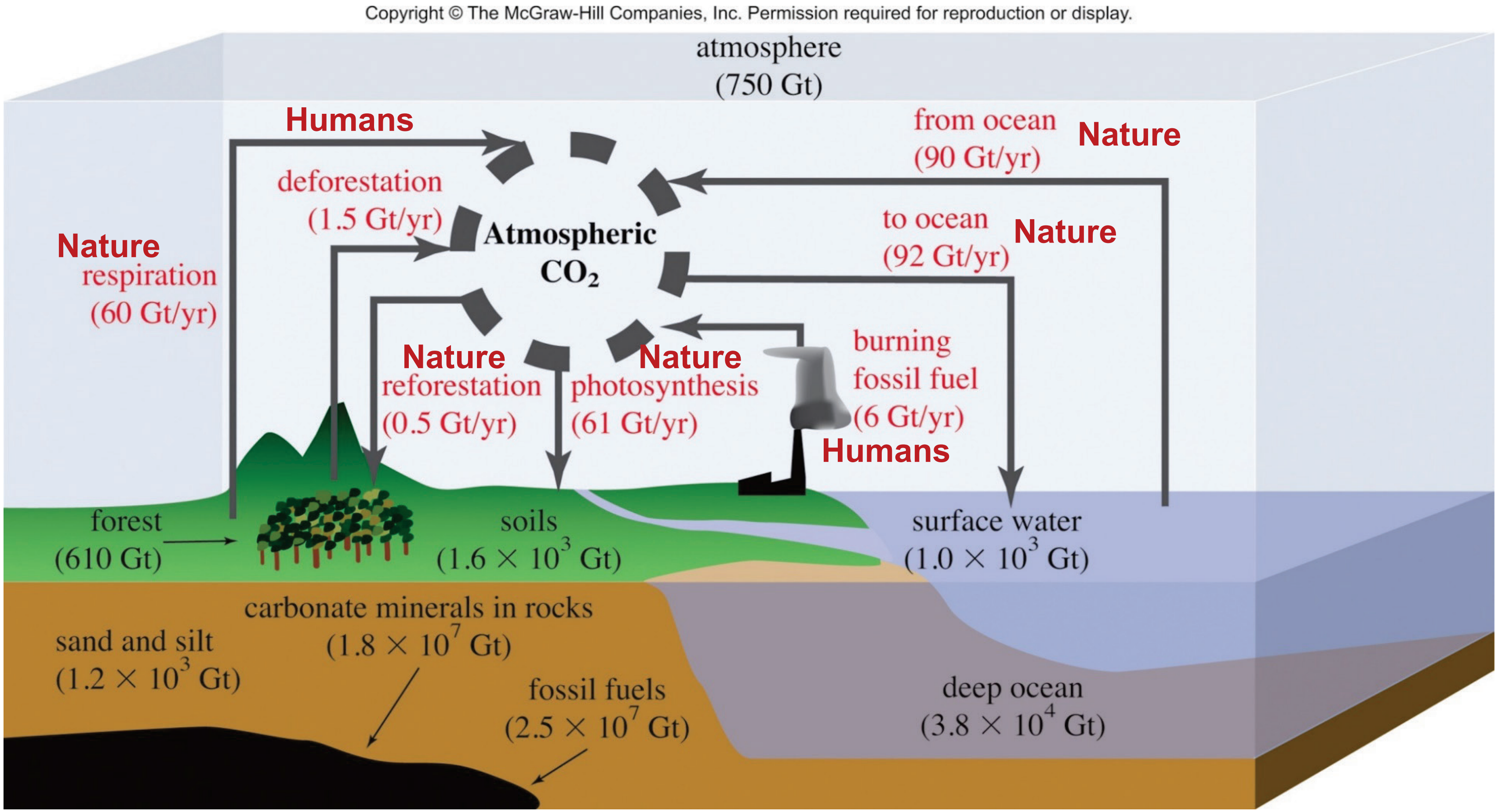


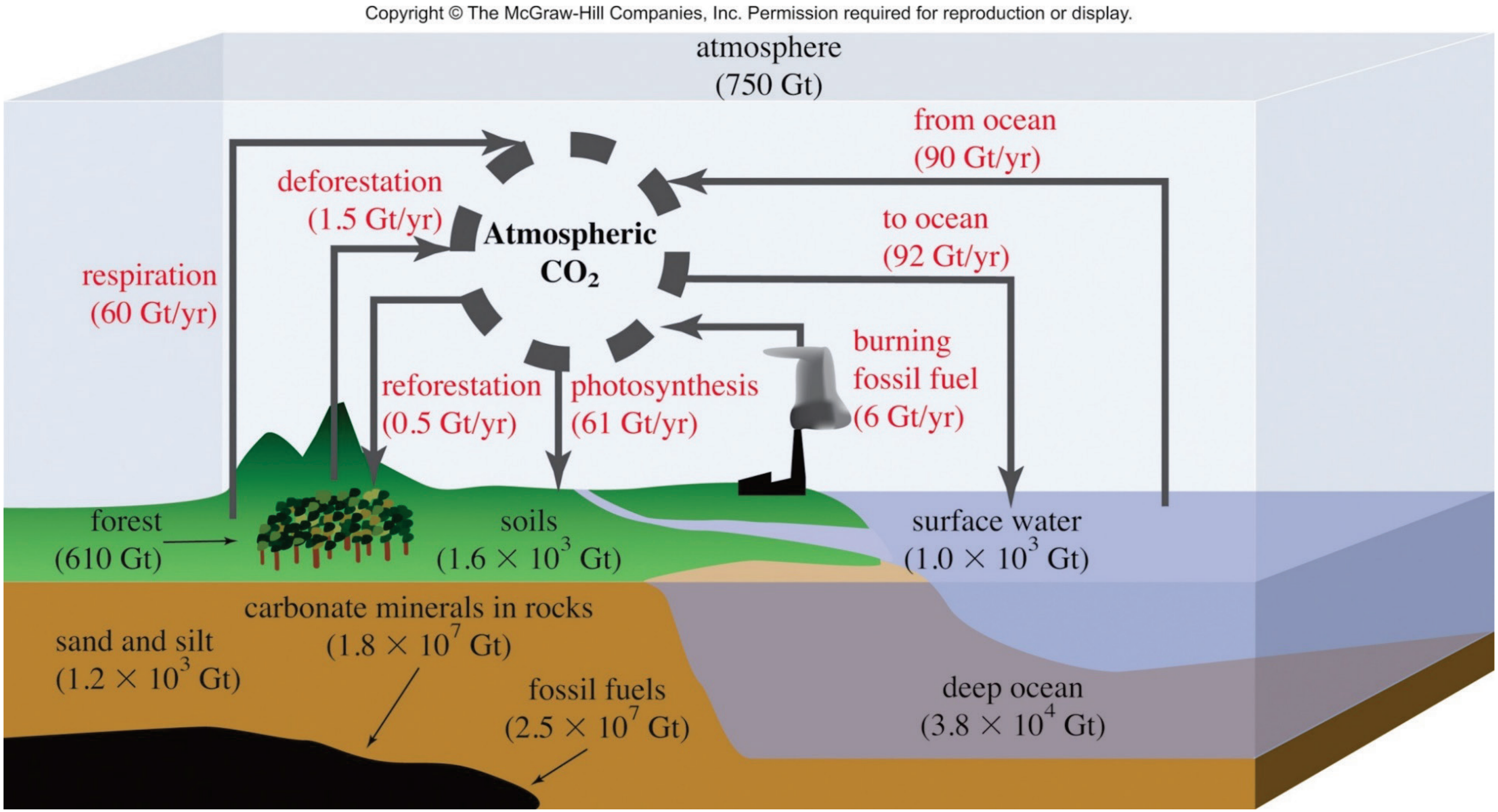
Fig 3.20, Chemistry in Context

CC:

Land Sink = (61 + 0.5) – (60) Gt C / yr = 1.5 Gt C / yr
Ocean Sink = 92 – 90 Gt C / yr = 2 Gt C / yr

In other words, ~3.5 Gt C / yr out of 7.5 Gt C / yr from burning fossil fuel & deforestation is being absorbed by world's oceans & terrestrial biosphere.

Global Carbon Cycle



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

Fig 3.20, Chemistry in Context

Ocean contains ~50 times more Carbon than the atmosphere, which is why oceanic processes are "the dog that wags the tail" [of atmospheric CO_2] on glacial to interglacial time scales

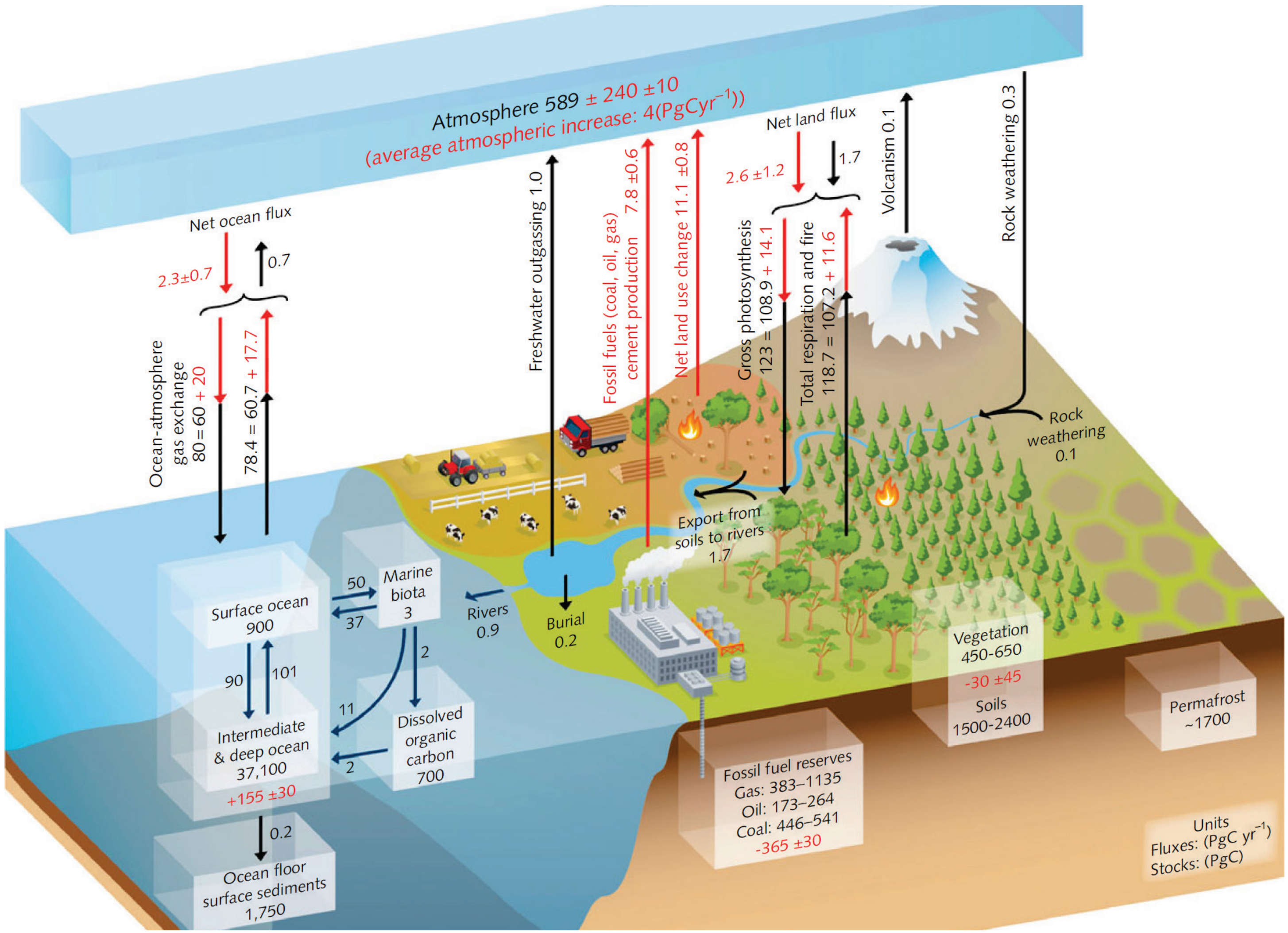
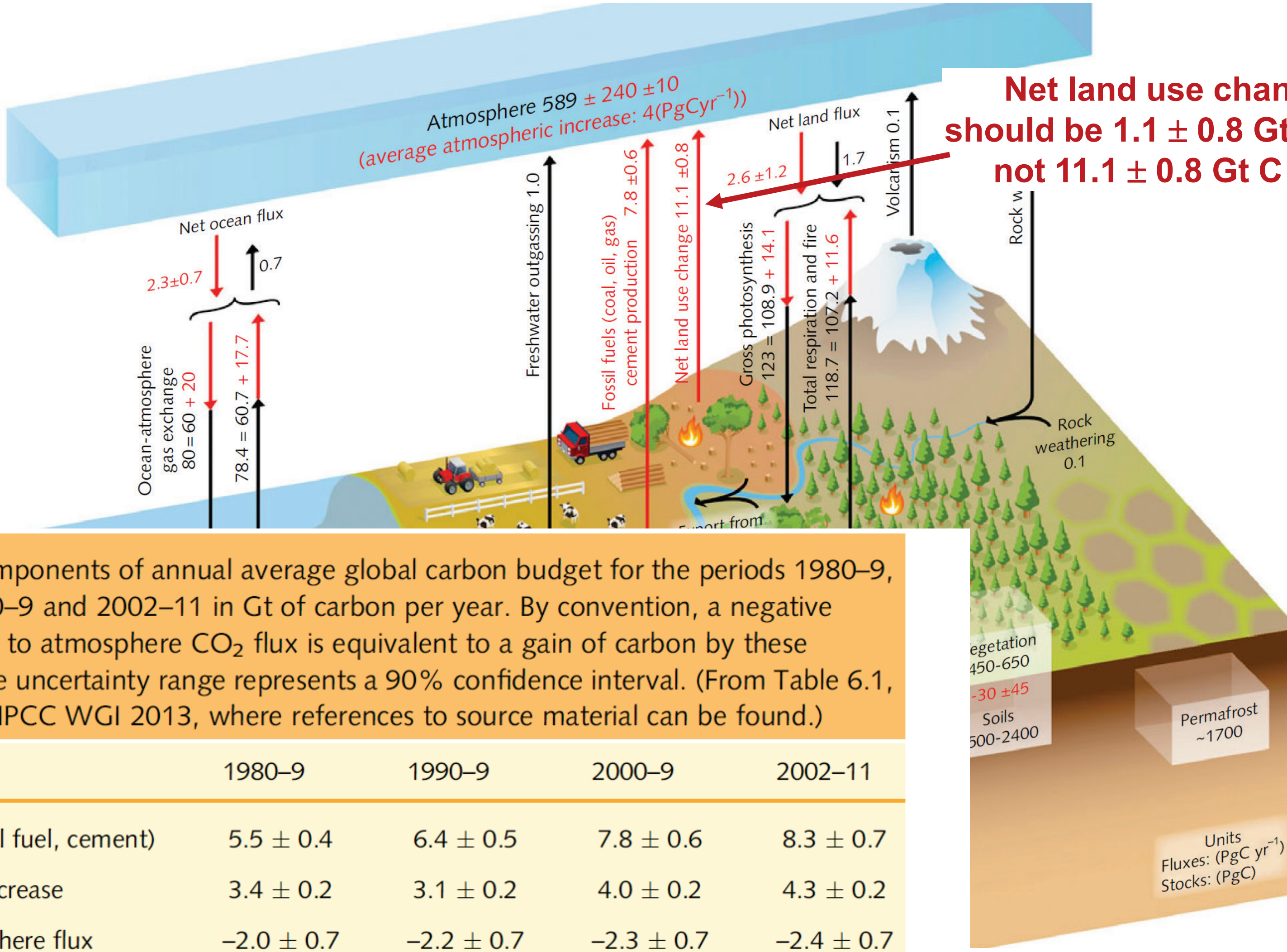


Fig 3.1, Houghton

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

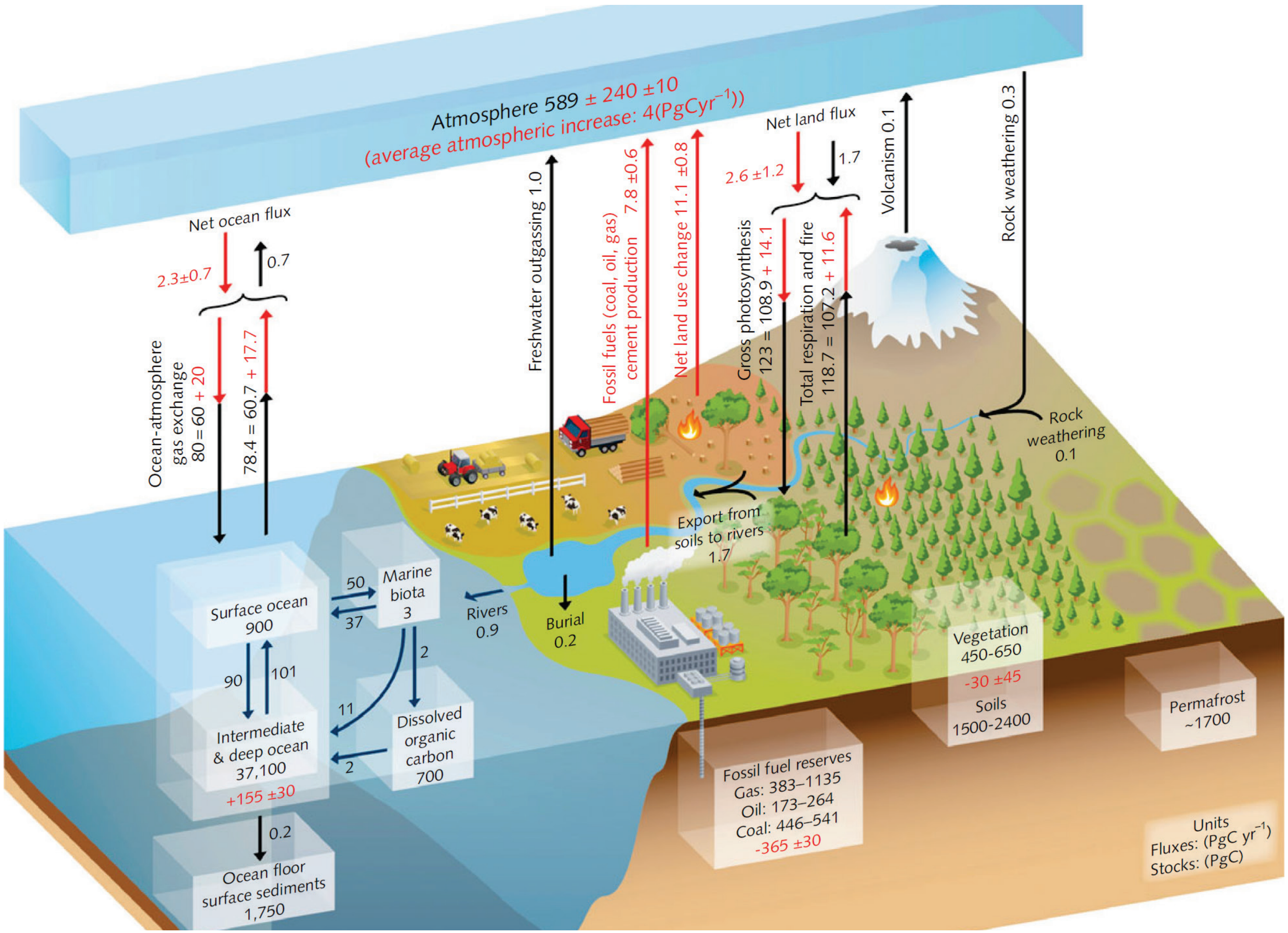


Net land use change should be 1.1 ± 0.8 Gt C / yr, not 11.1 ± 0.8 Gt C / yr

Table 3.1 Components of annual average global carbon budget for the periods 1980–9, 1990–9, 2000–9 and 2002–11 in Gt of carbon per year. By convention, a negative ocean or land to atmosphere CO_2 flux is equivalent to a gain of carbon by these reservoirs. The uncertainty range represents a 90% confidence interval. (From Table 6.1, Chapter 6 of IPCC WGI 2013, where references to source material can be found.)

	1980–9	1990–9	2000–9	2002–11
Emissions (fossil fuel, cement)	5.5 ± 0.4	6.4 ± 0.5	7.8 ± 0.6	8.3 ± 0.7
Atmospheric increase	3.4 ± 0.2	3.1 ± 0.2	4.0 ± 0.2	4.3 ± 0.2
Ocean–atmosphere flux	–2.0 ± 0.7	–2.2 ± 0.7	–2.3 ± 0.7	–2.4 ± 0.7
Land–atmosphere flux*	–0.1 ± 0.8	–1.1 ± 0.9	–1.5 ± 0.9	–1.6 ± 1.0
**Partitioned as follows*				
Land-use change	1.4 ± 0.8	1.5 ± 0.8	1.1 ± 0.8	0.9 ± 0.8
Residual land sink	–1.5 ± 1.1	–2.6 ± 1.2	–2.6 ± 1.2	–2.5 ± 1.3

Fig 3.1, Houghton



Houghton:

Land Sink = 2.6 ± 1.2 Gt C / yr

Ocean Sink = 2.3 ± 0.7 Gt C / yr

Fig 3.1, Houghton

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

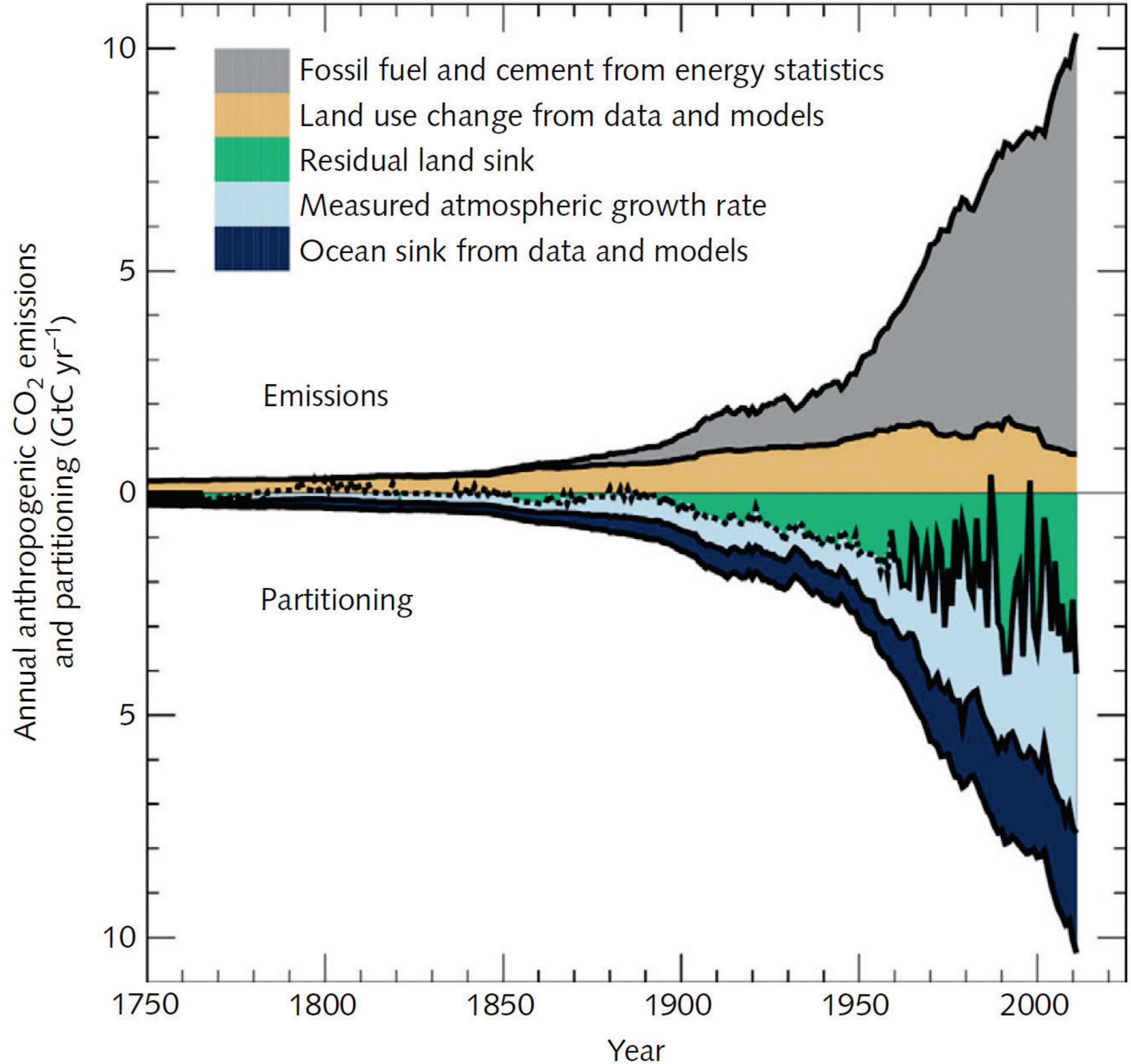


Fig 3.3, Houghton

Inferring CO_2 Uptake Based on ΔO_2

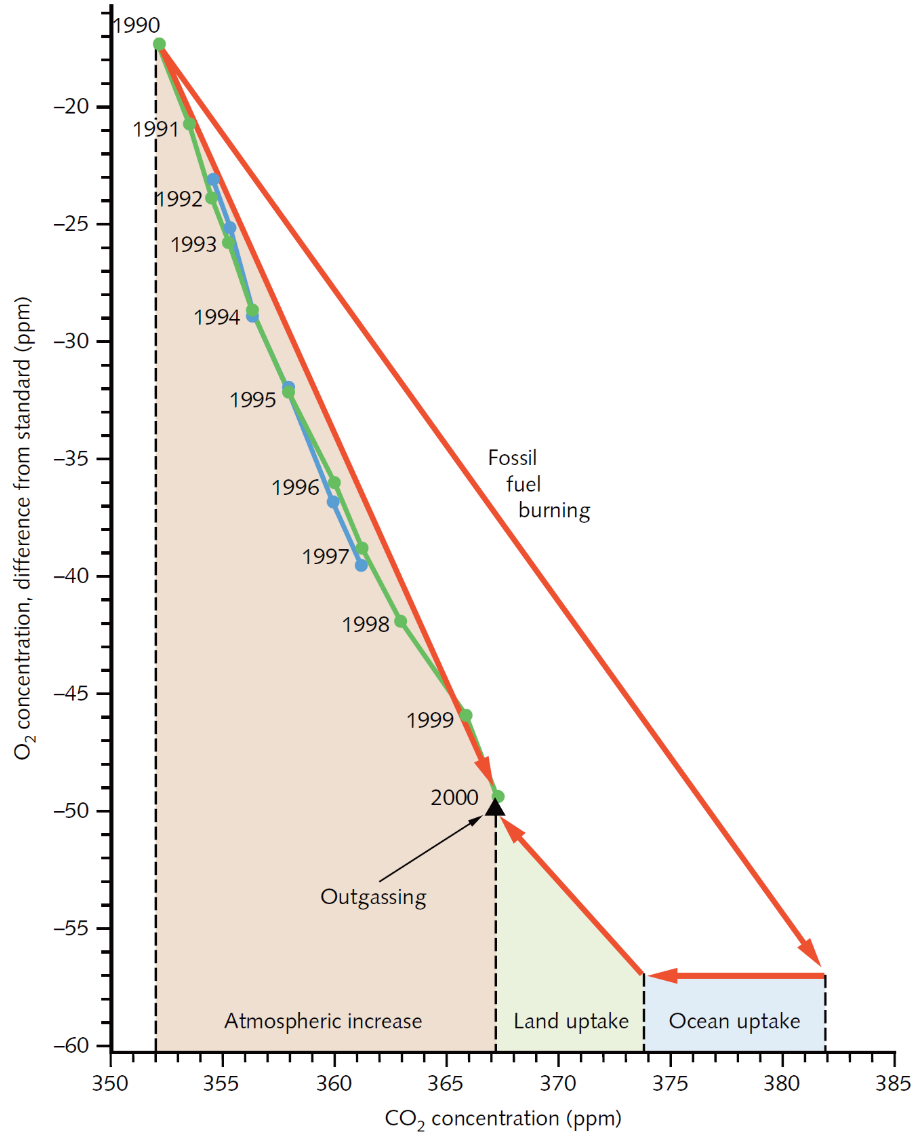
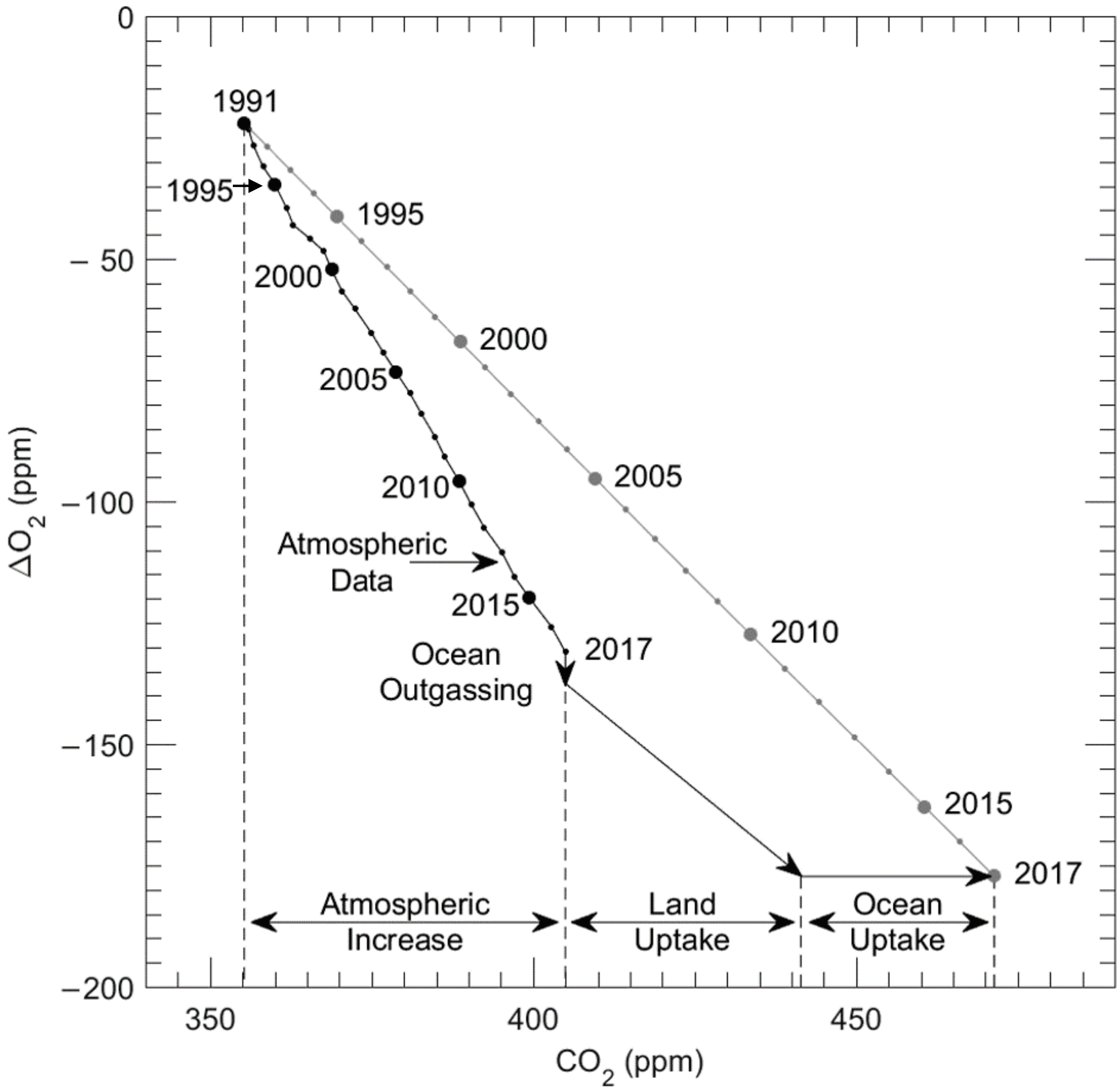


Fig 3.5, Houghton

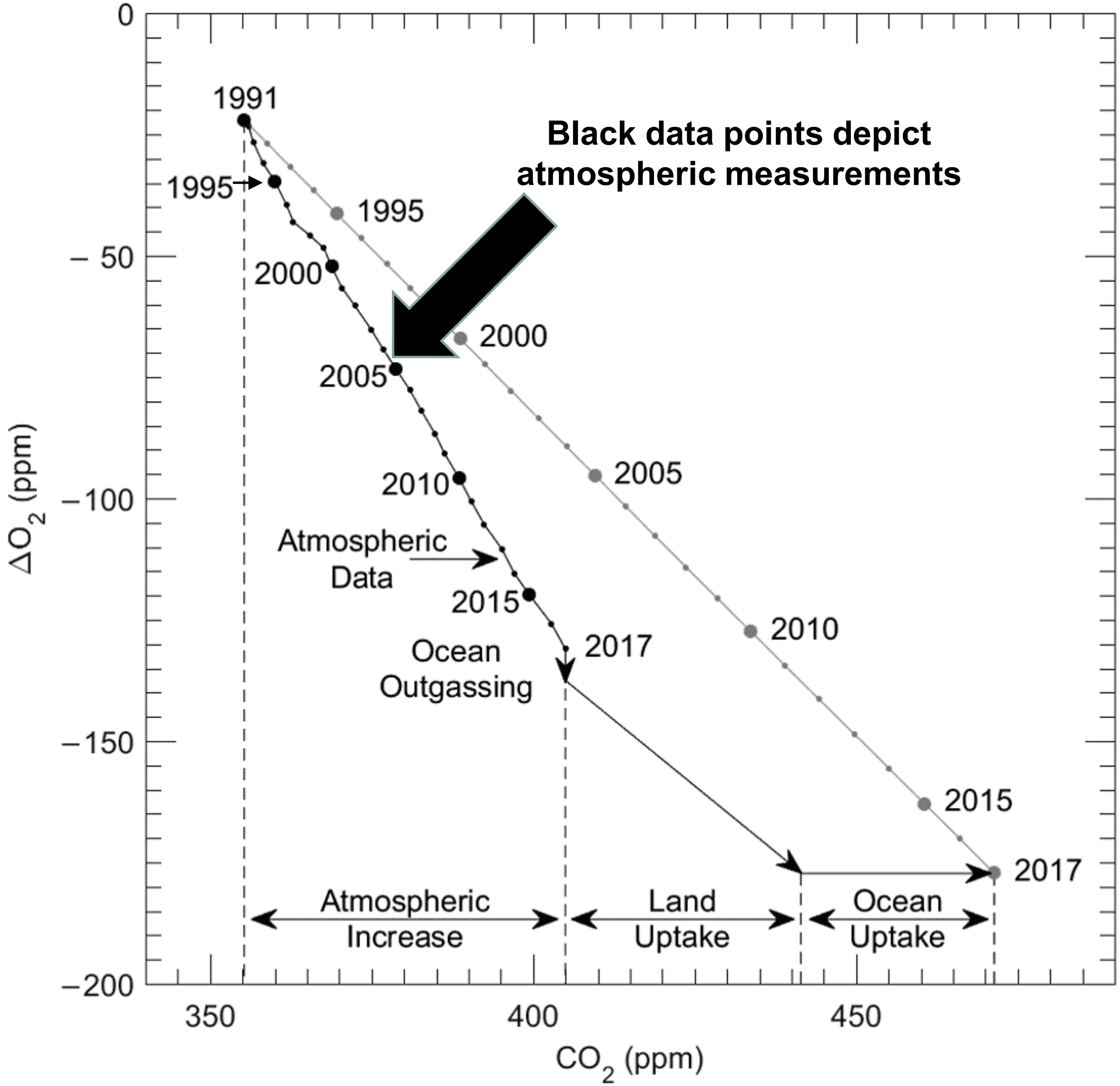
Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



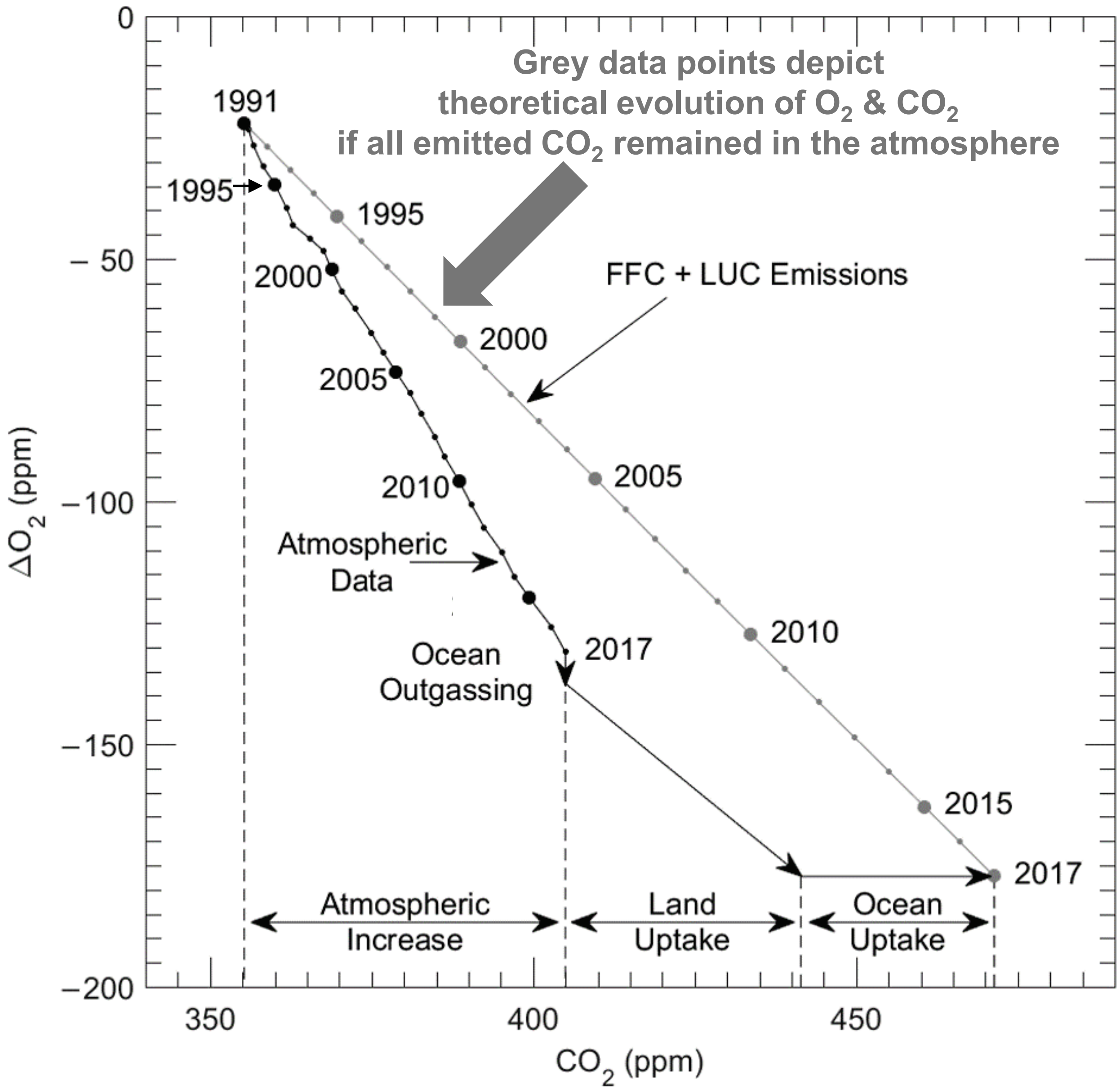
Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



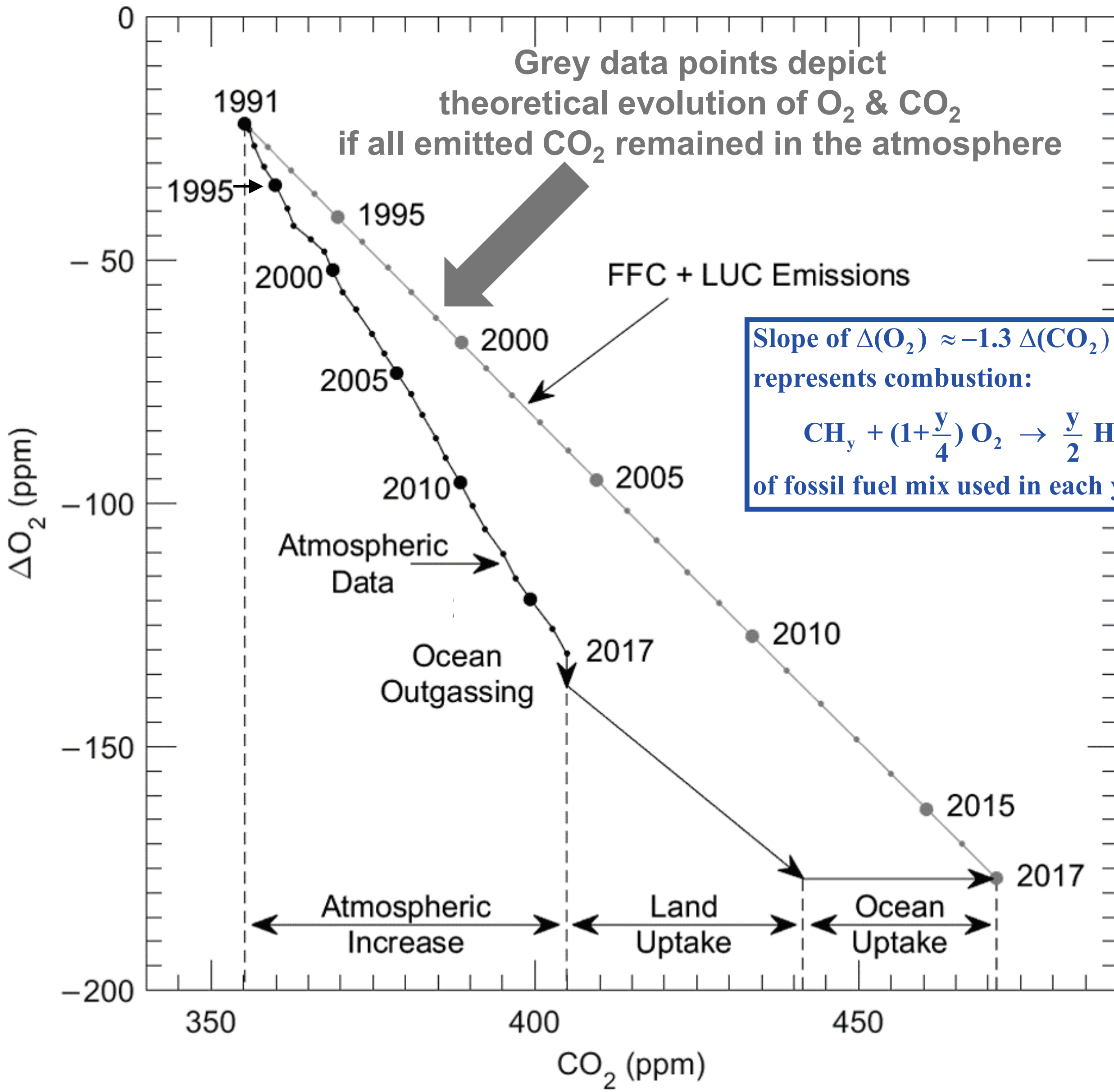
Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



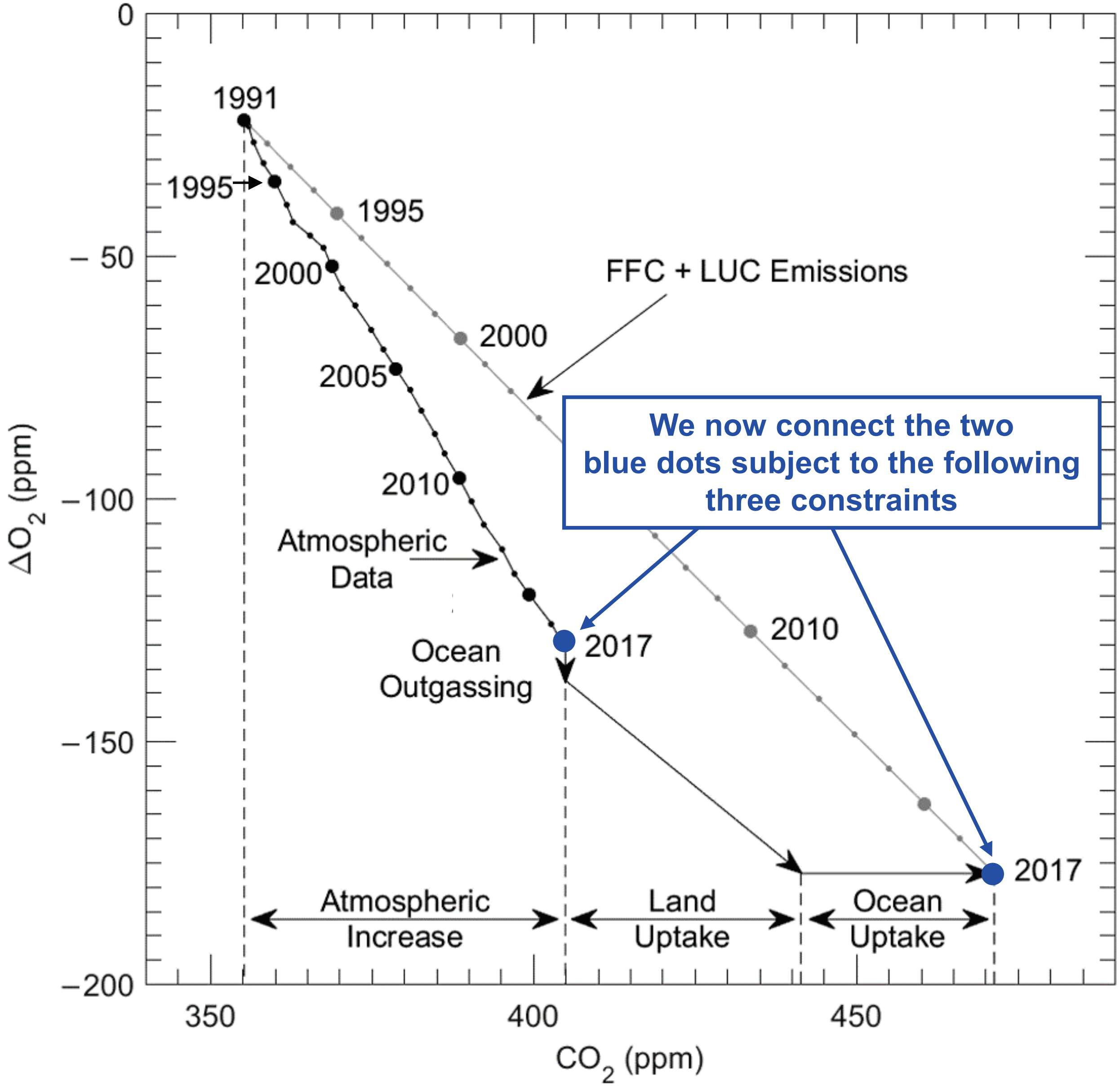
Slope of $\Delta(O_2) \approx -1.3\ \Delta(CO_2)$ represents combustion:

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

of fossil fuel mix used in each year.

Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
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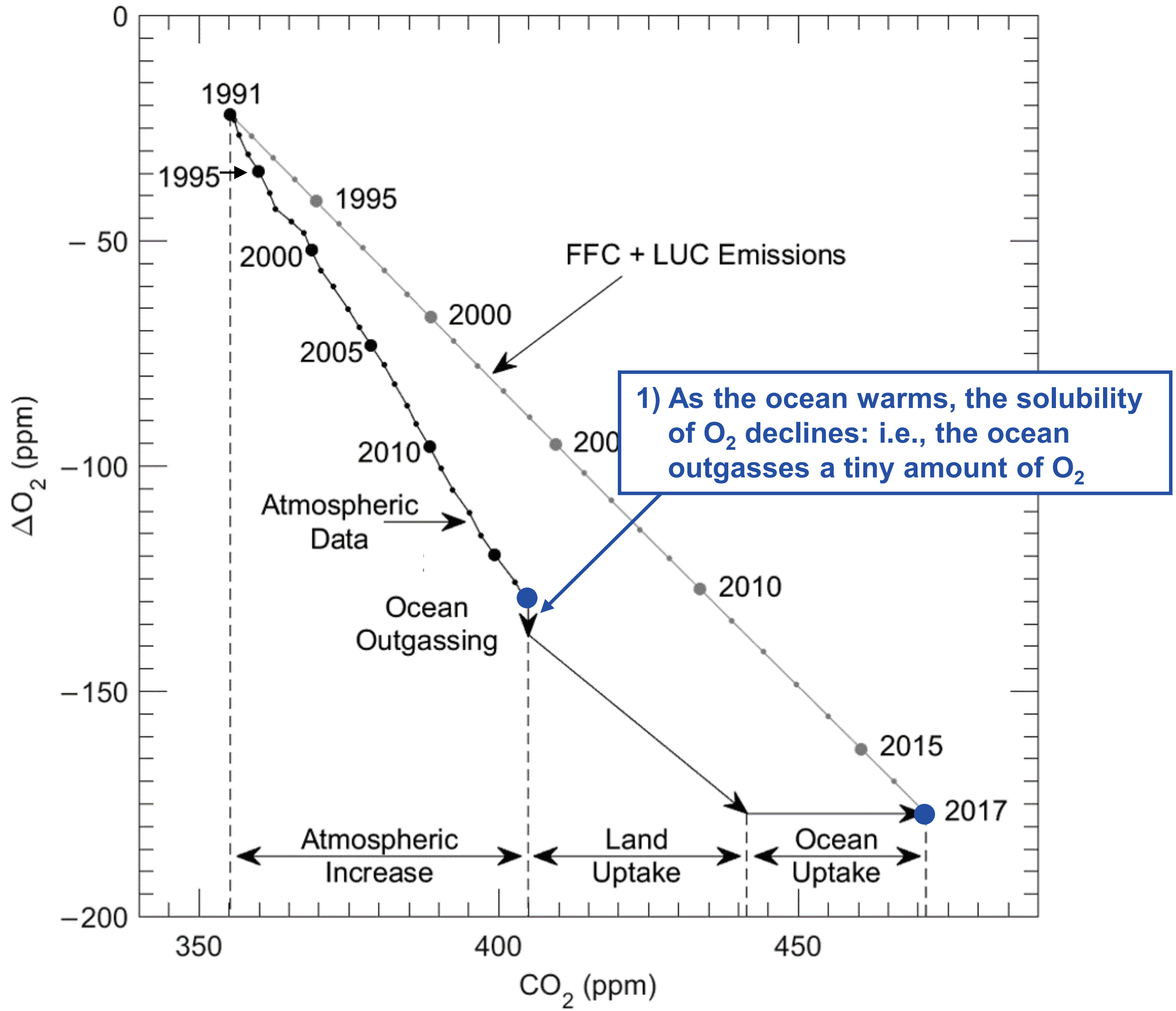
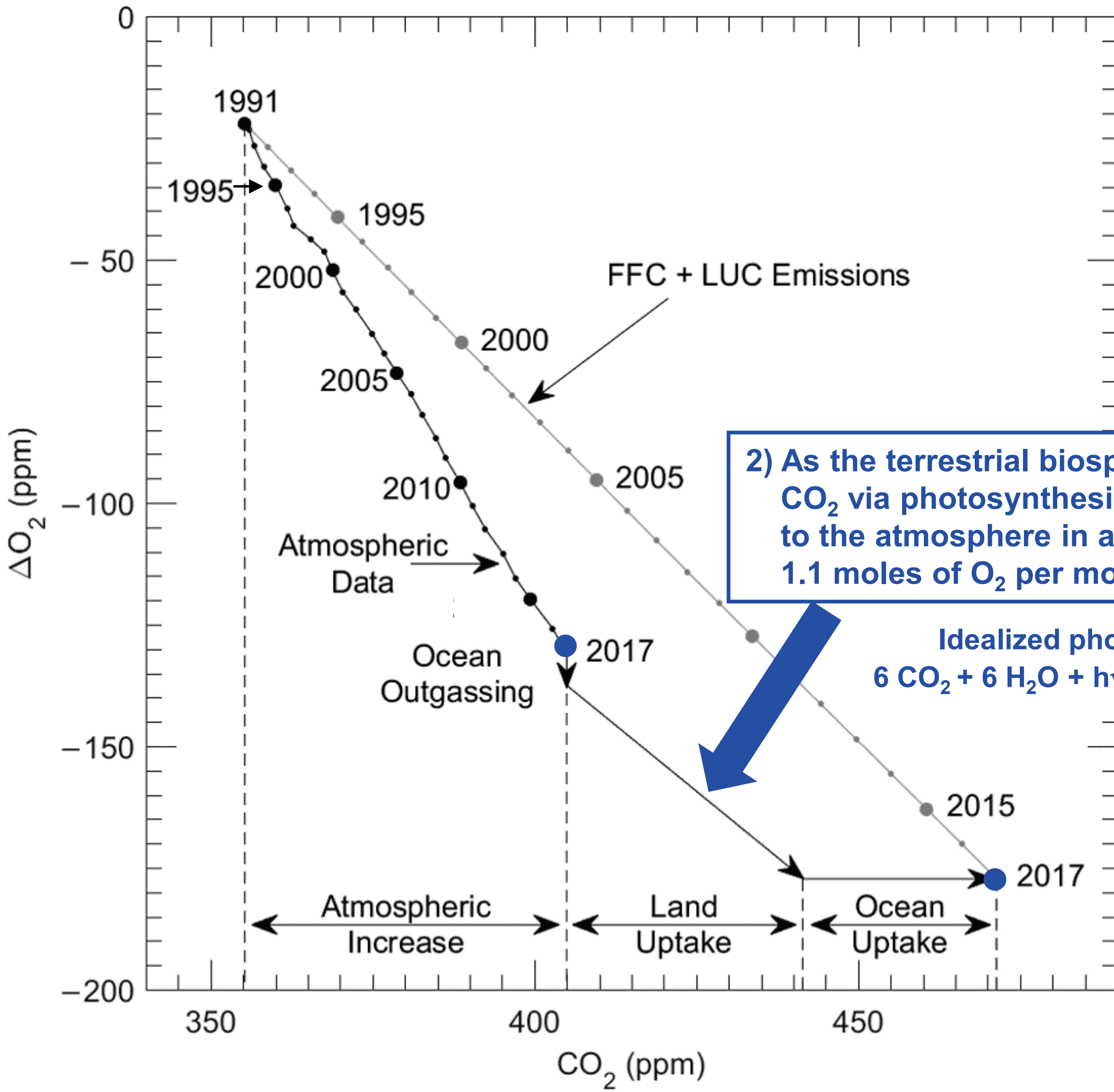


Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



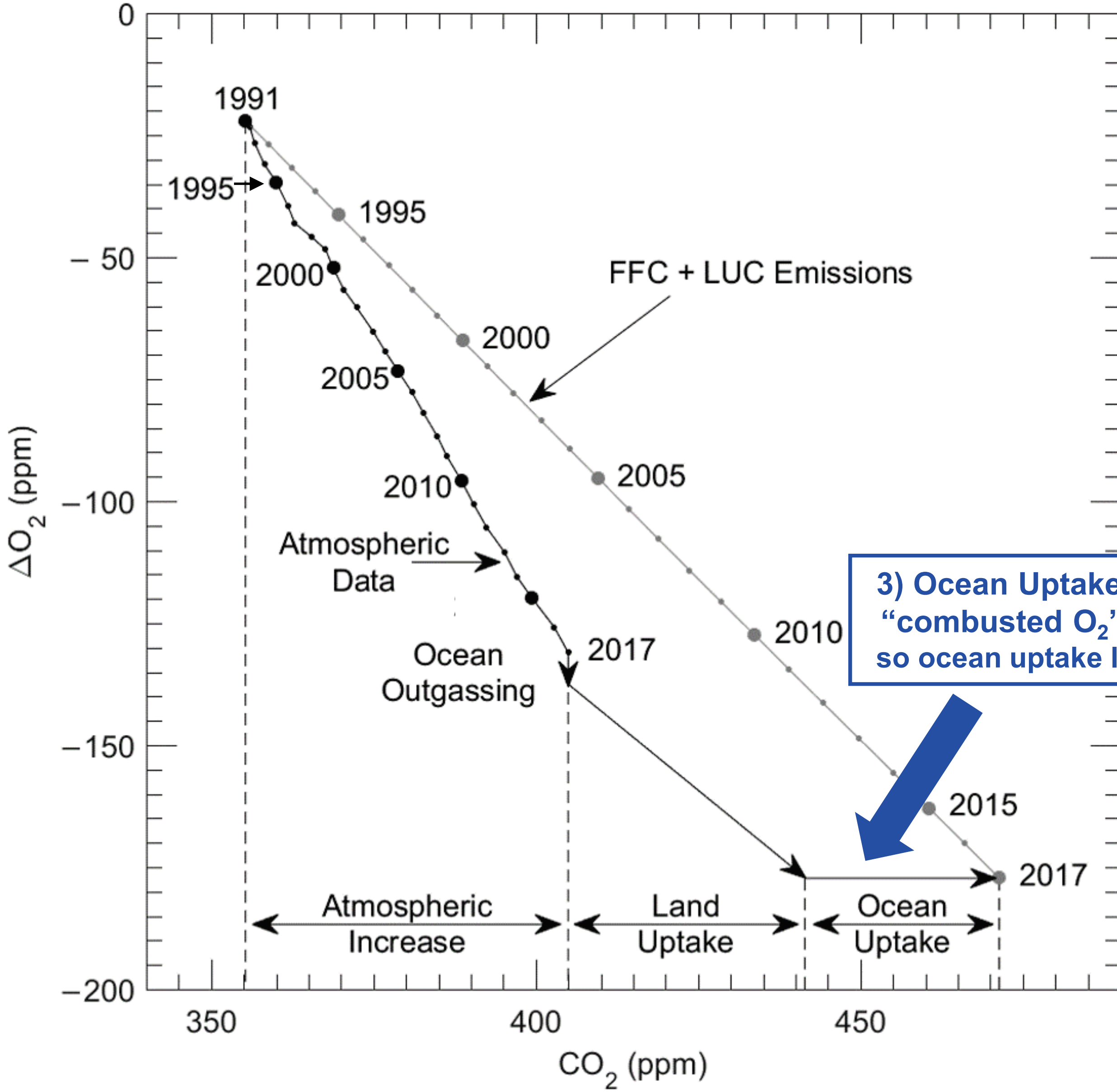
2) As the terrestrial biosphere uptakes CO_2 via photosynthesis, O_2 is returned to the atmosphere in a molar ratio of 1.1 moles of O_2 per mole of CO_2

Idealized photosynthesis:

$$6\ CO_2 + 6\ H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6O_2$$

Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



3) Ocean Uptake does not return "combusted O_2" to atmosphere, so ocean uptake line has slope of 0

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

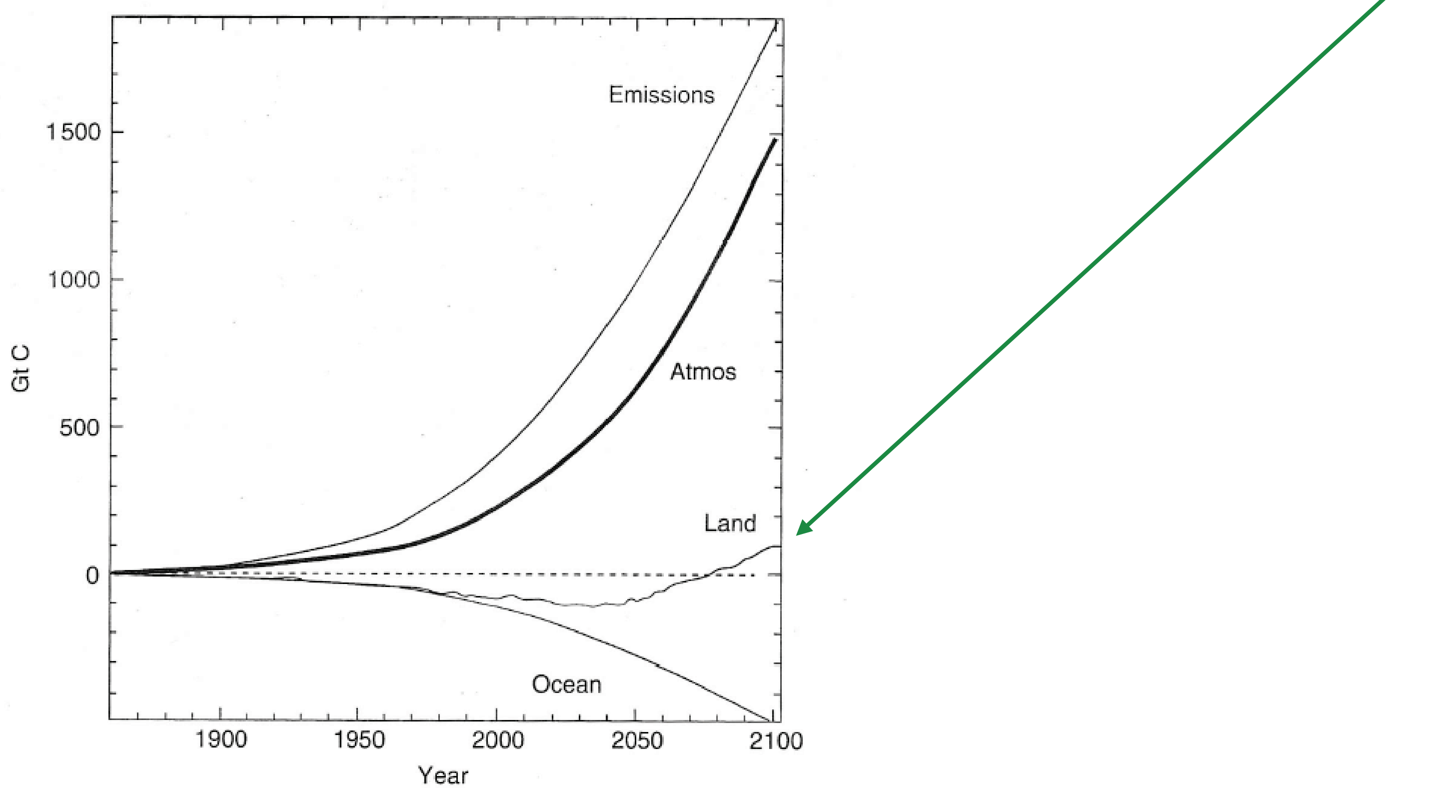


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

Figure 3.5, Houghton 3d Edition

Uptake of Atmospheric CO_2 by Trees (Land Sink)

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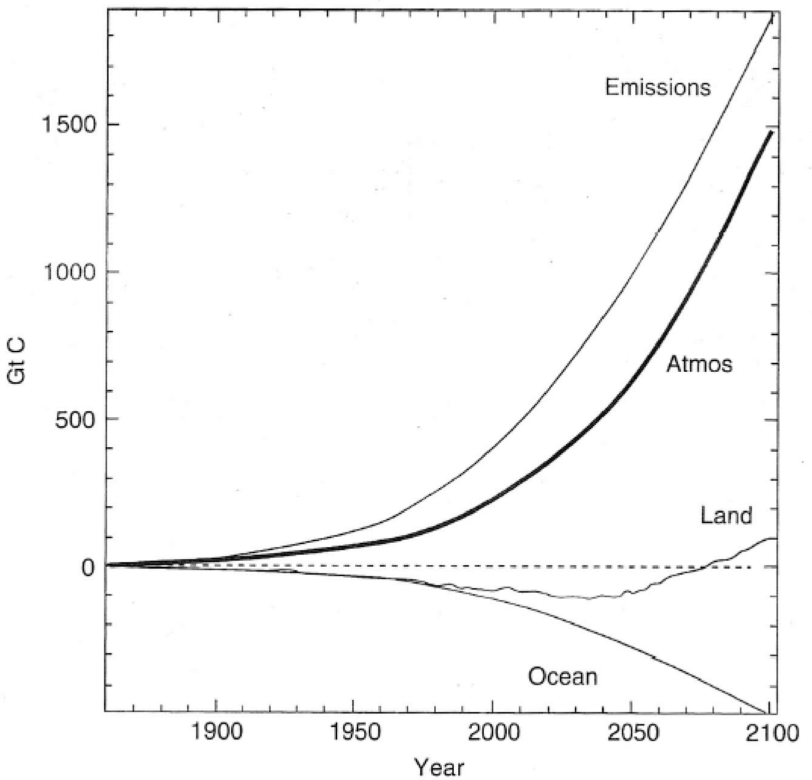
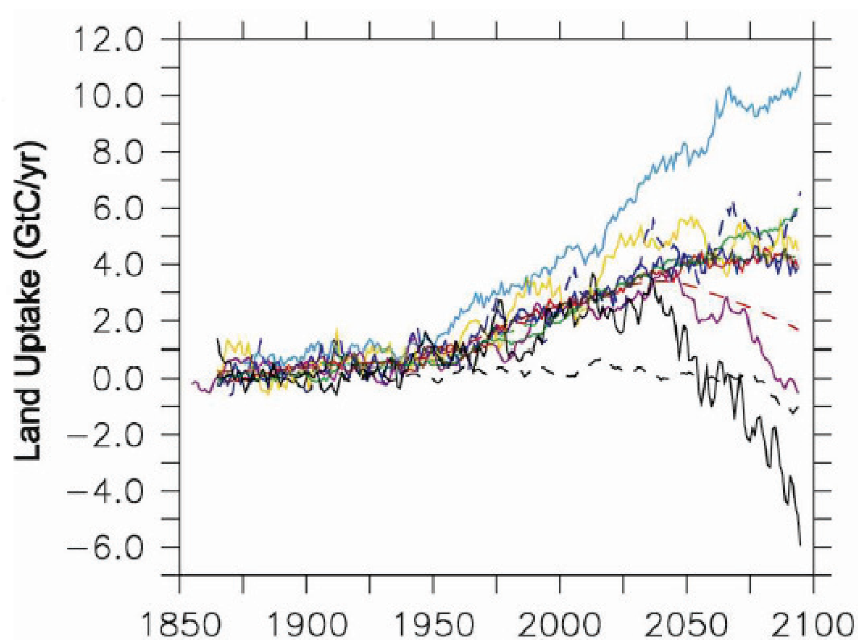


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

Figure 3.5, Houghton 3d Edition

- 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**

The carbon dioxide fertilisation effect is an example of a biological feedback process. It is a negative feedback because, as carbon dioxide increases, it tends to increase the uptake of carbon dioxide by plants and therefore reduce the amount in the atmosphere, decreasing the rate of global warming.

Page 43, Houghton

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 empirically in a greenhouse setting because ?

The results of this study suggest that competition for light was the major factor influencing community composition, and that CO_2 influenced competitive outcome largely through its effects on canopy architecture. Early in the experiment competition for nutrients was intense.

Fakhri A. Bazzaz, 1990: https://www.jstor.org/stable/pdf/2097022.pdf

Many Free-Air Carbon dioxide Enrichment (FACE) experiments have been developed, throughout the world including a new experiment in Brazil, to attempt to understand how the terrestrial biosphere will respond to rising levels of atmospheric CO_2

http://aspenface.mtu.edu

https://www.nature.com/news/polopoly_fs/1.12855!/menu/main/topColumns/topLeftColumn/pdf/496405a.pdf?origin=ppub

https://www.nature.com/scitable/knowledge/library/effects-of-rising-atmospheric-concentrations-of-carbon-13254108

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

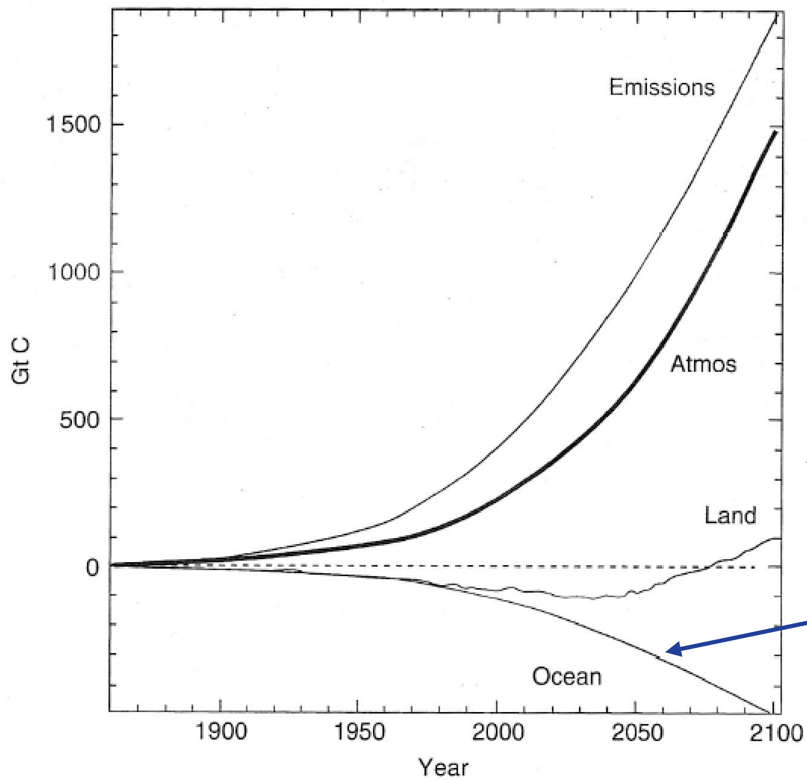


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

Ocean sink: relatively long lived reservoir

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

Figure 3.5, older (Third) edition of Houghton

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	411 ppm Present Day	560 ppm 2 × Pre-Indus.
Ocean Carbon	2020×10^{-6} M	2079×10^{-6} M	2122×10^{-6} M
$[HCO_3^-]$	1771×10^{-6} M	1882×10^{-6} M	1958×10^{-6} M
$[CO_2\,(aq)]$	9.13×10^{-6} M	13.4×10^{-6} M	18.3×10^{-6} M
$[CO_3^{2-}]$	239×10^{-6} M	148×10^{-6} M	146×10^{-6} M
pH	8.32	8.18	8.06

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

Notes:

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

M ≡ mol/liter

Mathematics supporting this calculation on Extra Slides 1 to 3 of Class Notes.

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Ocean is slightly basic

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Ocean acidity rises as Atmospheric CO_2 increases

CC: "A decrease of 0.1 pH unit corresponds to a 26% increase in the amount of H+ in seawater"

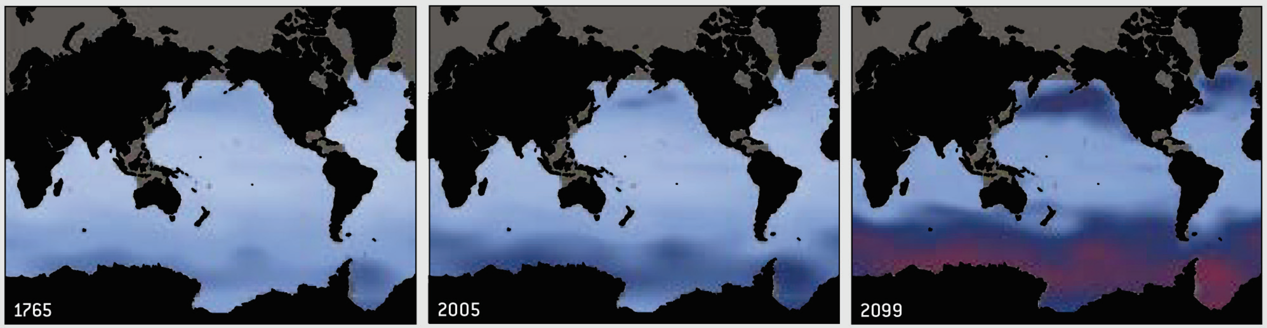
Uptake of Atmospheric CO_2 by Oceans

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

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

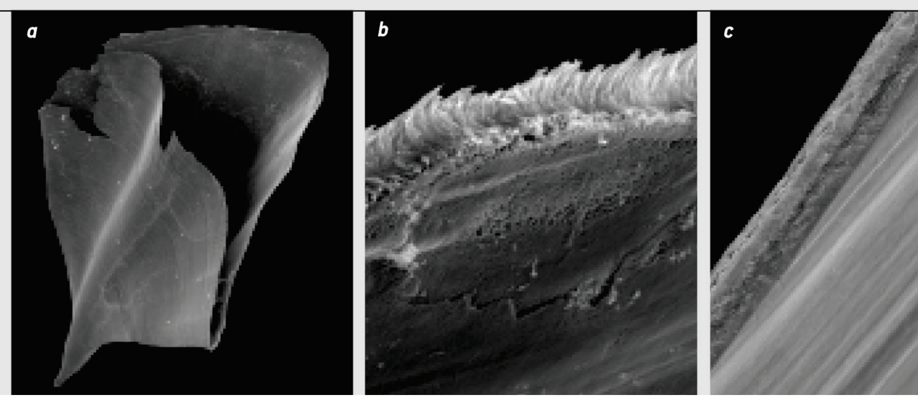
THE (RAGGED) FUTURE OF ARAGONITE

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 Oceans

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pH	8.32	8.18	8.06

Revelle Factor:

$$\frac{\Delta \text{Atmos}_{CO2}}{\langle \text{Atmos}_{CO2} \rangle_{AVERAGE}} = \frac{131 \text{ ppm}}{0.5 \times (411 + 280) \text{ ppm}} = \mathbf{0.34}$$

$$\frac{\Delta \text{Ocean Carbon}}{\langle \Delta \text{Ocean Carbon} \rangle_{AVERAGE}} = \frac{59 \times 10^{-6} \text{ M}}{0.5 \times (2020 + 2079) \times 10^{-6} \text{ M}} = \mathbf{0.029}$$

Pre-industrial to present: Ocean carbon rose by 2.9% for a 34% increase in atmospheric CO_2

Uptake of Atmospheric CO_2 by Oceans

When CO_2 dissolves:

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pH	8.32	8.18	8.06

Revelle Factor:

$$\frac{\Delta \mathrm{Atmos}_{CO2}}{\langle \mathrm{Atmos}_{CO2} \rangle_{AVERAGE}} = \frac{149\ \mathrm{ppm}}{0.5 \times (560 + 411)\ \mathrm{ppm}} = \mathbf{0.31}$$

$$\frac{\Delta \mathrm{Ocean\ Carbon}}{\langle \Delta \mathrm{Ocean\ Carbon} \rangle_{AVERAGE}} = \frac{43 \times 10^{-6}\ \mathrm{M}}{0.5 \times (2079 + 2122) \times 10^{-6}\ \mathrm{M}} = \mathbf{0.020}$$

Present to a future we hope to avoid: Ocean carbon will rise by 2.0% for a 31% increase in atmospheric CO_2

Extra Slides to Follow

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 = 411 ppm:

$$[CO_2(aq)] = 3.4 \times 10^{-2}\ M / atm\ 4.11 \times 10^{-4}\ atm = 1.397 \times 10^{-5}\ M$$

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)

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 $p_{CO2} = 1.397 \times 10^{-5}$ M for present atmosphere

$[H^+]\,[HCO_3^-] = K_1\,[CO_2(aq)] = 4.3 \times 10^{-7}\ M \times 1.397 \times 10^{-5}\ M = 6.01 \times 10^{-12}\ M^2$

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

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

$[H^+]\,[H^+] = 6.01 \times 10^{-12}\ M^2$ ⇨ $[H^+] = 2.451 \times 10^{-6}$ M

pH $= -\log_{10}[H+] =$ ***5.61*** (411 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, 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 $[\mathrm{CO_3^{2-}}]$ 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 $[\mathrm{CO_2(aq)}]+[\mathrm{HCO_3^-}]+[\mathrm{CO_3^{2-}}]$.

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