12.842 / 12.301 Past and Present Climate
Fall 2008

12.842
Climate Physics and Chemistry
Fall 2008

Natural and Fossil Fuel CO_2 in the Ocean (II)

Outline:

- Estimating gas exchange rates
  - Thin film model
  - Piston velocity
  - Wind speed dependence
- Ocean CO_2 exchange
  - Global CO_2 exchange rate
  - Air-sea disequilibrium and spatial variability
- Estimating the penetration of ocean surface waters into the deep ocean
  - Ocean circulation primer
  - Transient tracers
- Estimating ocean uptake of fossil fuel CO_2: is there a "missing sink"?
- The $\Delta O_2/\Delta CO_2$ method for estimating ocean and biospheric fossil fuel uptake: quantifying the "missing sink"
- Other methods for observing fossil fuel CO_2 uptake
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Estimating Ocean of Fossil Fuel CO_2 Uptake

- CO_2 in the atmosphere equilibrates with the ocean mixed layer on a timescale of less than a year. Hence this is not a rate-limiting step because the mean age of fossil-fuel CO_2 is ~28 years.
- The rate-limiting step is the penetration of surface waters into the interior of the ocean.
- In order to estimate ocean CO_2 uptake, we need to find out how fast surface waters move into the deep sea.

Ocean Surface Currents: schematic

Image removed due to copyright restrictions.
Citation: Figure 3-13. Major features of the surface circulation of the oceans.
McLellan, 1965: opposite p. 42.

Surface circulation of the North Atlantic Ocean from drifters

Image removed due to copyright restrictions.
Citation: N. Atl. surface drift 1990s.jpg: Fratantoni, D. M. "North Atlantic Surface Circulation During the 1990's Observed with Satellite-tracked Drifters." *J Geophys Res* 106 (2001): 22067-22093.

Western North Atlantic Potential Temperature Section

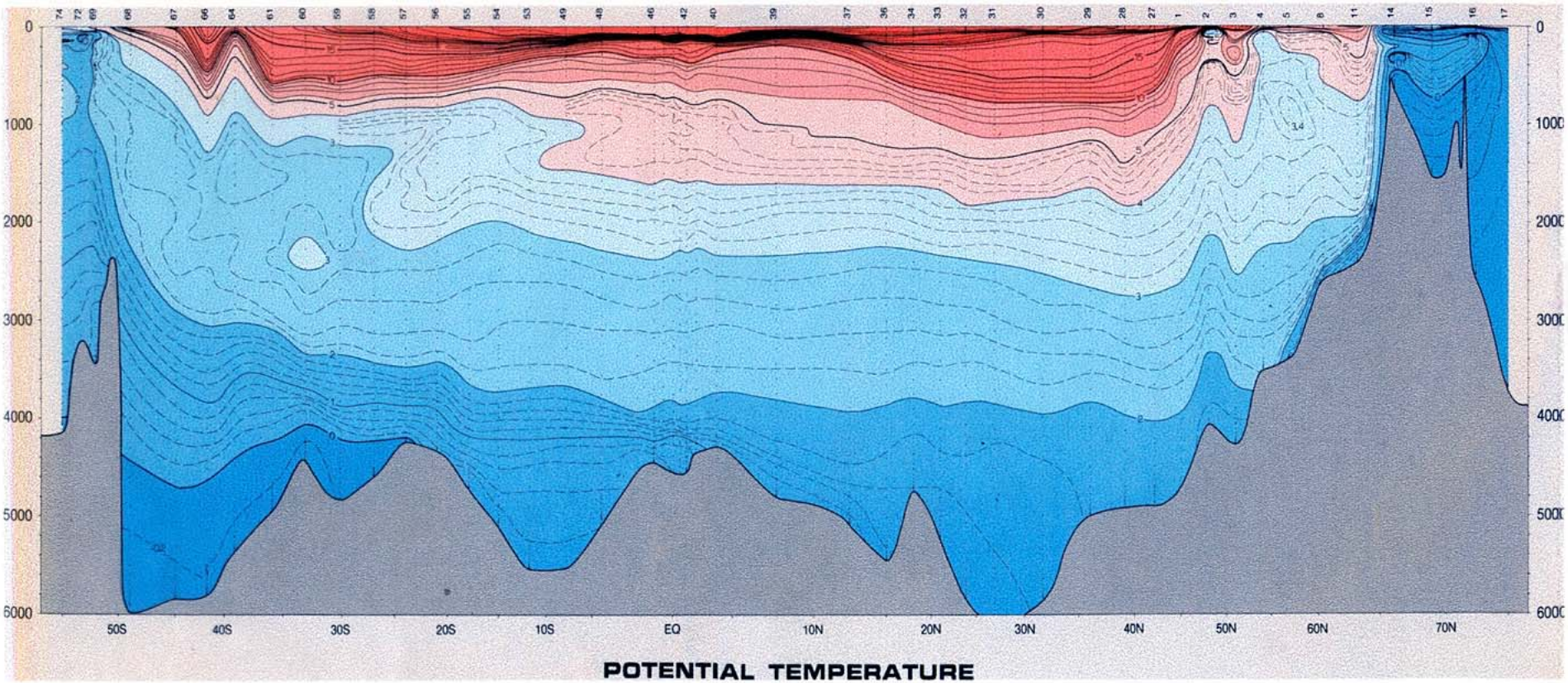
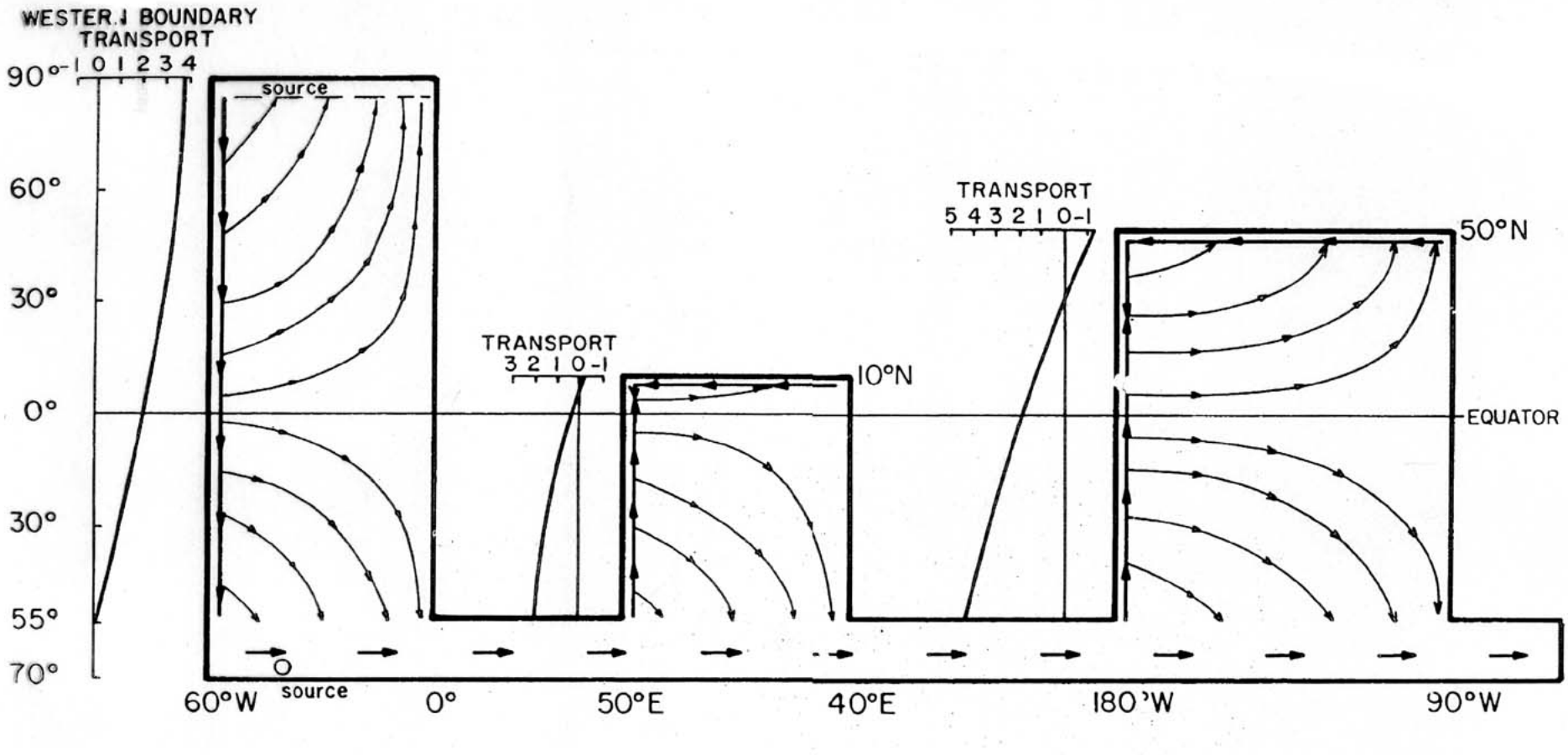


Image courtesy of US Government.

- *This experiment, which seem'd first but mere food for curiosity, became in the interim very useful to us. By its means we supplied our cold bath, and cooled our wines or water at our pleasure; which is vastly agreeable to us in this burning climate.*

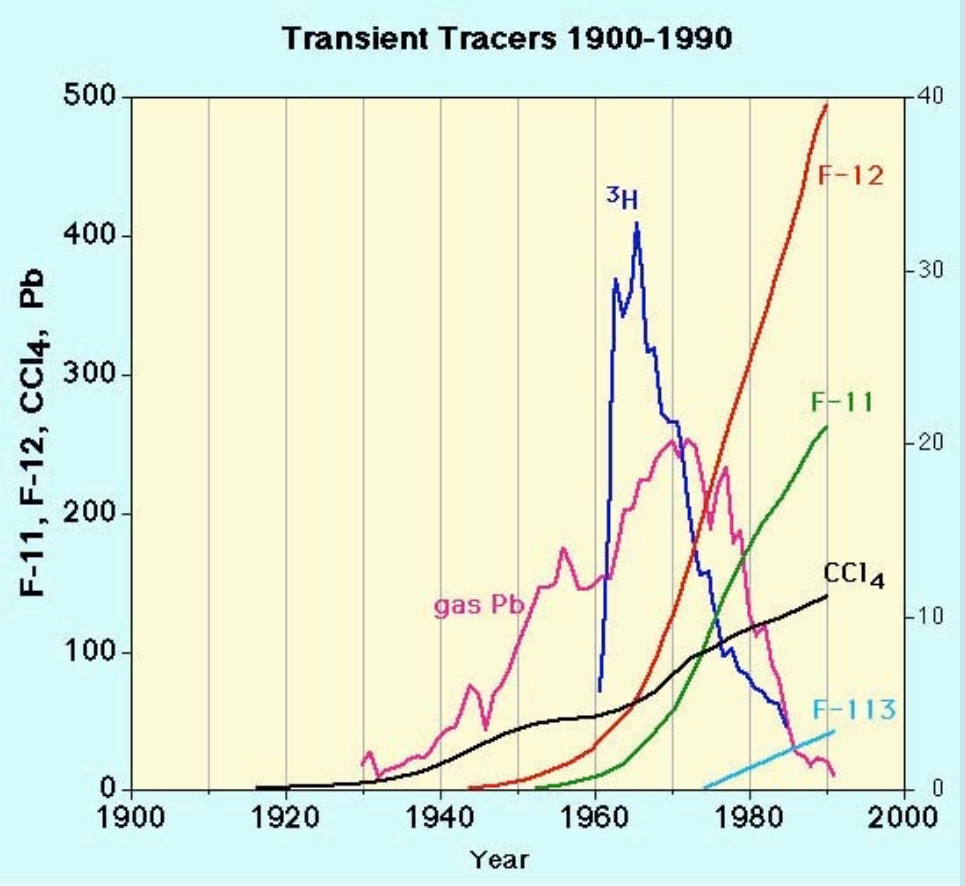
Ellis (1751)

Stommel and Arons Deep Ocean Circulation Scheme: western boundary currents, slow interior recirculation



Transient Tracers

- Other substances have been added to the atmosphere and surface ocean in the recent past: bomb tritium (^3H) and ^{14}C, and chlorofluorocarbons (CFCs). The difference between these tracers and CO_2 is that they begin entering into an ocean where there did not previously exist (or at very low concentrations). We can then use these substances to estimate how much of the ocean has been in contact with the surface in recent years.

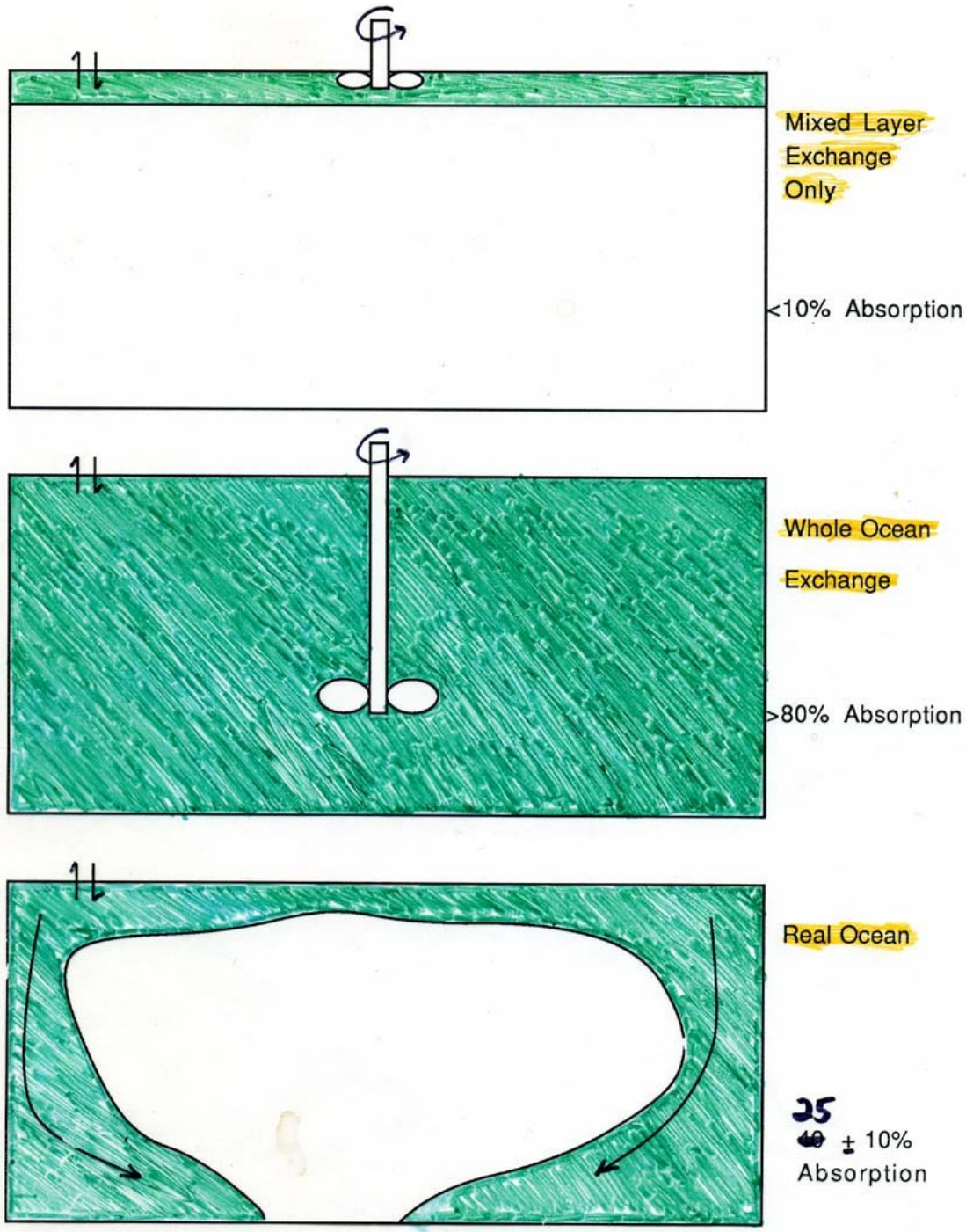


Tritium in the North Atlantic Ocean

Image removed due to copyright restrictions.
Citation: Ostlun, H. G., and C. G. H. Rooth. "The North Atlantic Tritium and Radiocarbon Transients 1972-1983." *J Geophys Res* 95 (1990): 20147-20165.

CFC 11 in the North Atlantic Ocean

Image removed due to copyright restrictions.
Citation: Image of Atlantic CFC-11 section. Doney, S. C., and J. L. Bullister.
"A Chlorofluorocarbon Section in the Eastern North Atlantic." *Deep-Sea Res* 39 (1992): 1857-1883.



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

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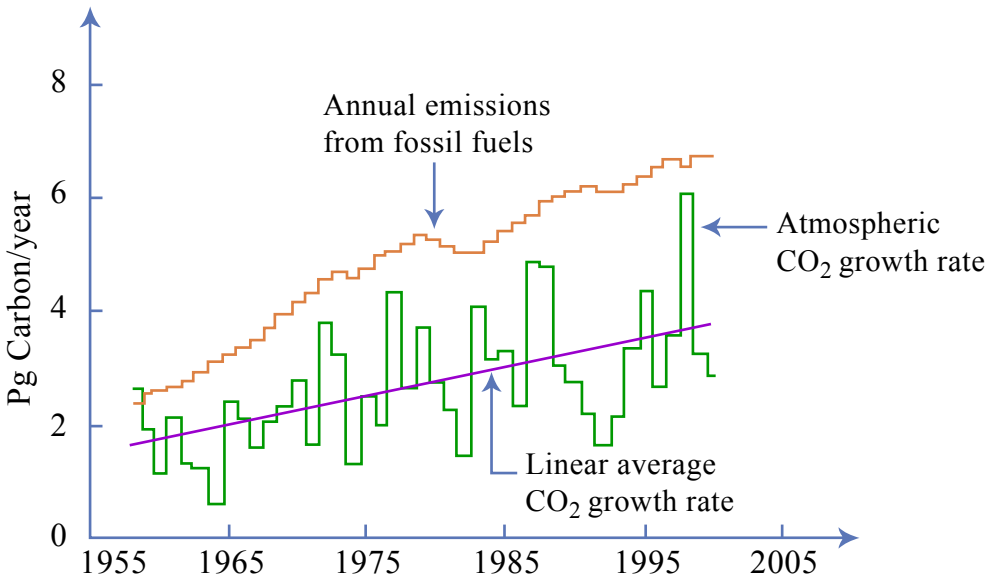
Calculating the ocean fossil fuel CO_2 uptake: Step 1: subtract out the steady state natural cycle



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

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

Calculating the ocean fossil fuel CO_2 uptake: Step 2: calculate the mean age of fossil fuel CO_2

- The concept of mean age works as if we were to attach a clock to every atom of CO_2 emitted (set to zero at the time of emission), then at some later point gather in all the clocks and calculate the average.

$$Mean\,Age = \frac{\int_{-t}^{0} -tF(t)dt}{\int_{-t}^{0} F(t)dt}$$

where t = 0 is the present

and F(t) = CO_2 emissions

The mean age of CO_2 at present is about 28 years

Calculating the ocean fossil fuel CO_2 uptake: Step 3: calculate CO_2 inventories in 1962 and 1990

- *Units: 10^{15} moles of carbon*

	thickness	1962	1990	1990-1962
Atmosphere		60	66	6.0
Mixed layer	75m	50	50.5	0.5
Upper Ocean	300m	200	202	2.0
Bottom Water	112m	75	75.8	0.8
Total				9.3
% taken up by ocean:		3.3/9.3 =	35%	

However, note that we will present evidence that the continental biosphere is taking an amount of carbon comparable to that taken up by the ocean. In that event, the % taken up by the ocean is 3.3/12.6 = 26%

Table 1. IPCC global CO, budget for 1980-1989 [as adapted from *(38)* by (56)].

Reservoir	Average flux (Gt of *C year*$^{-1}$)
Sources	
Fossil fuels	5.4 ± 0.5
Deforestation and land use	1.6 ± 1.0
Total	7.0 ± 1.2
Sinks	
Atmosphere	3.2 ± 0.1
Oceans (modeled uptake)	2.0 ± 0.8
Total	5.2 ± 0.8
Imbalance (sources - sinks)	1.8 ± 1.4

Other ways to estimate ocean CO_2 uptake

- CO_2 influx/efflux estimate (from Δp_{CO2})
- Loss of oxygen from the atmosphere
- $\delta^{13}C$ of oceanic CO_2 (because fossil fuels are ~ -27‰ compared to ~0‰ for the ocean) O_2 influx/efflux estimate (from Δp_{CO2})
- "excess CO_2" calculation based on ocean CO_2 and nutrient data

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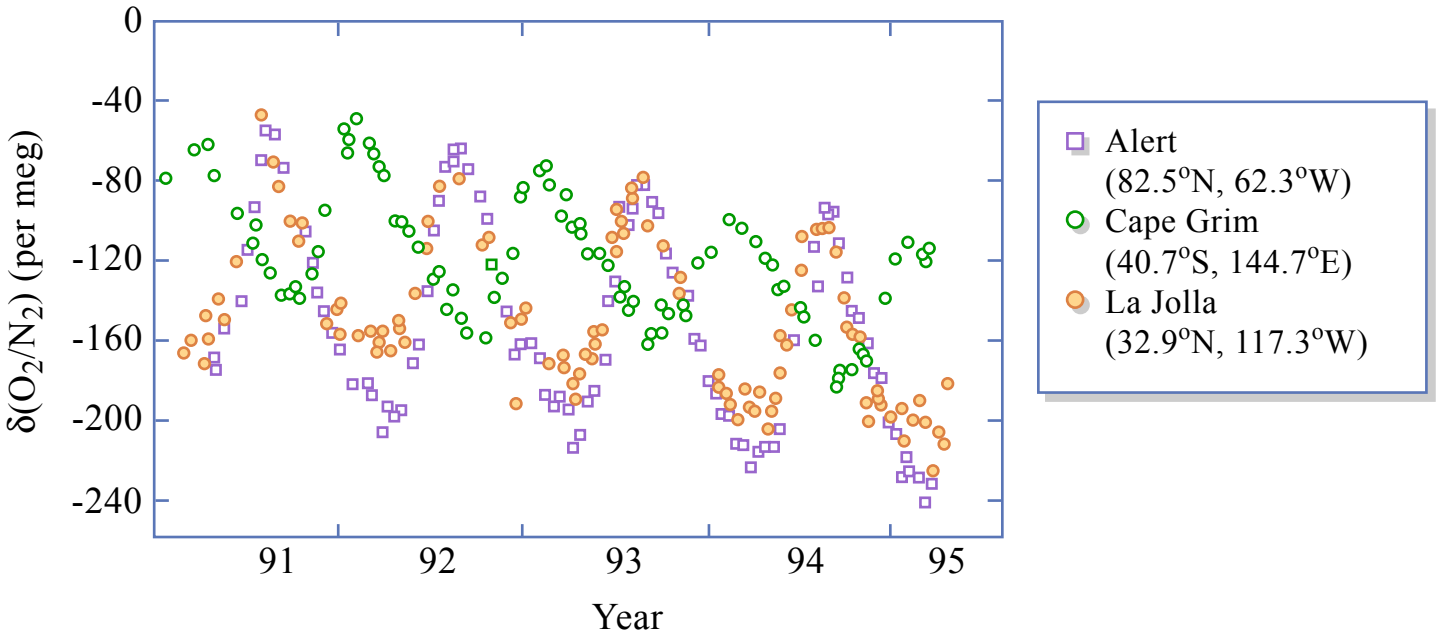
Atmospheric O_2 decrease, 1991-1995



$\delta(O_2/N_2)$ of air samples collected at Alert, La Jolla and Cape Grim and measured using the interferometric method.

Figure by MIT OpenCourseWare based on *Nature* Vol. 381, 1996.

Source: Keeling et al., 1996.

Oxygen changes in the atmosphere

a. When fossil fuel is burned, O_2 is consumed.

b. O_2 in atmosphere is 201,000 ppmV where CO_2 is ~385 ppmV. So a ~10% rise in atmospheric CO_2 is matched by an ~0.03% fall in oxygen! Hence oxygen must be measured with extreme precision (parts per million).

c. O_2/CO_2 ratio depends on fuel composition:, e.g.

$CH_4 + 2O_2 = CO_2 + 2H_2O$, but
$CH_2O + O_2 = CO_2 + H_2O$

d. CO_2 dissolving in the ocean doesn't change atmospheric O_2, but net CO_2 uptake into the biosphere releases O_2 - so here is a way to separate ocean CO_2 uptake from biospheric CO_2 uptake.

e. Ralph Keeling (Keeling Jr.) uses interferometry to measure changes in the refractive index of air (which depends on O_2 concentration) to measure changes in atmospheric O_2 to the required precision. The O_2/N_2 ratio can be measured almost as well by mass spectrometry as well (Michael Bender).

Atmospheric ΔCO_2-ΔO_2 vector diagram

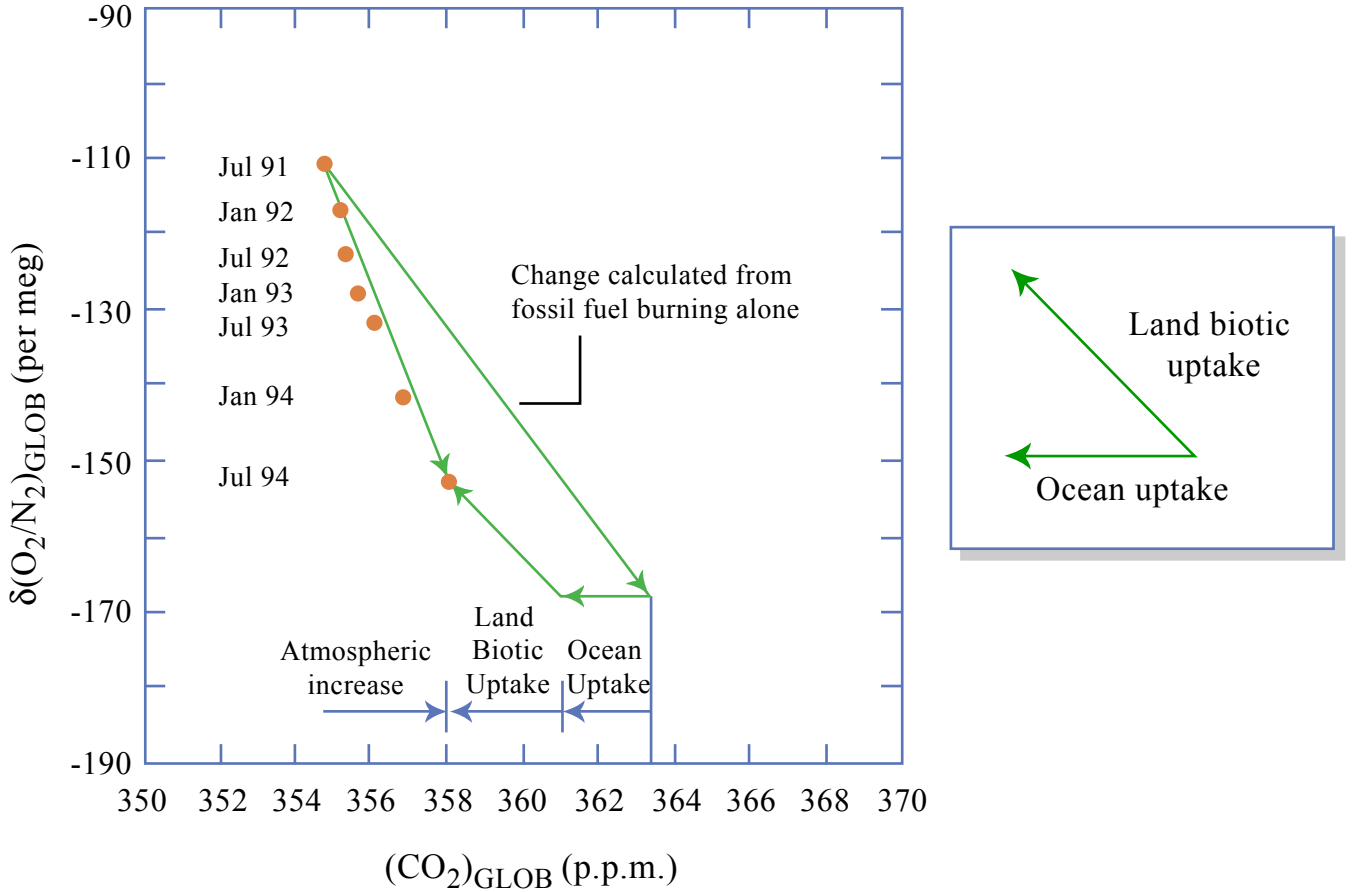


Figure by MIT OpenCourseWare based on Keeling, et al., 1996.

Source: R. Keeling lab

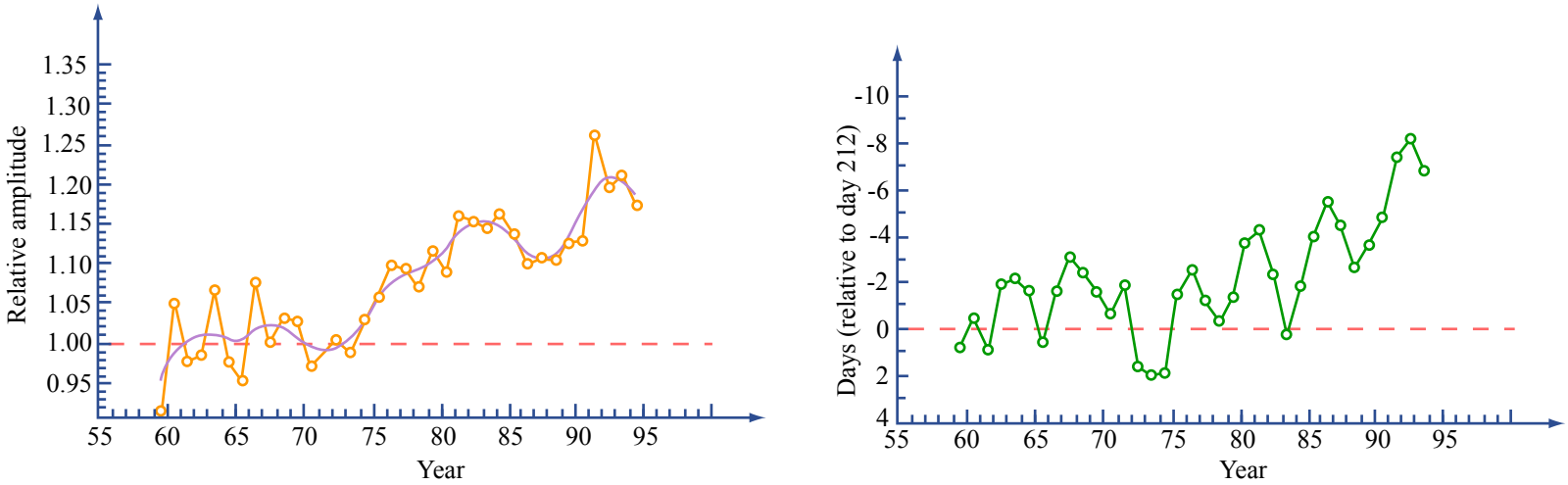
Another O_2-CO_2 time series

Image removed due to copyright restrictions.
Citation: Figure 1. Battle, Bender, and Tans, et al. *Science* 287 (March 31, 2000): 2467.

Using O_2 and carbon isotopes to estimate fossil fuel CO_2 uptake

Image removed due to copyright restrictions.
Citation: Figure 4. Battle, Bender, and Tans, et al. *Science* 287 (March 31, 2000): 2467.

Increasing amplitude and length of the growing season



Trends in relative amplitude and timing of the seasonal cycle of atmospheric CO_2. *a*, At Mauna Loa Observatory, Hawaii. Annual values of the amplitude (Left plot, dots connected by orange lines) were determined from weekly averaged continuous concentration data[15] fitted annually to a phase-locked 4-harmonic seasonal function. This function together with a linearly increasing gain factor, was first established by a fit to the full record[3], after which the gain was redetermined separately for each year. The linearly increasing gain factor, referenced to 1964, was computed to be 0.675 + 0.045% per year. A smoothing spline[19] (Purple curve, with standard error, σ_A, of 0.028%) shows quasi-decadal changes in the relative amplitude. The timing of the downward zero crossing of the seasonal cycle (Right plot, dots connected by solid line segments), was obtained from 3-year fits to the CO_2 record.

Figure by MIT OpenCourseWare.

*Source: Keeling and Chin (1996) Nature **382**, 146-149.*

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Atmospheric $\delta^{13}C$ of CO_2, 1976-1995

Image removed due to copyright restrictions.
Citation: Figure 13. Keeling, et al. *Glob Biogeochem Cycles* 10 (1996): 335.

Image removed due to copyright restrictions.

Temperature-dependent carbon isotope equilibration with the ocean: now and pre-anthropogenic

Changing $\delta^{13}C$ of the ocean due to fossil fuel uptake

Image removed due to copyright restrictions.
Citation: Figure 1 and Figure 2. Quay, P. D., B. Tilbrook, and C. S. Wong. *Science* 256 (April 3, 1992): 74-79.

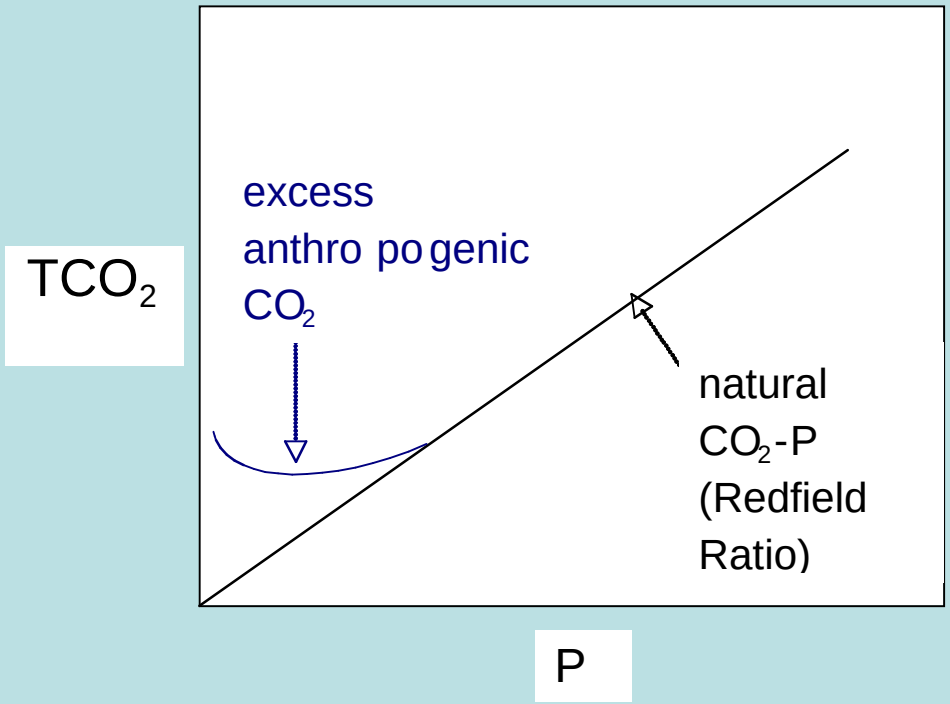
Evolving Pacific Ocean $\delta^{13}C$ depth profiles

Image removed due to copyright restrictions.
Citation: Figure 3. Quay, P. D., B. Tilbrook, and C. S. Wong
Science 256 (April 3, 1992): 74-79.

Using ice core CO_2 and tree-ring $\delta^{13}C$ data to estimate anthropogenic carbon emissions

Image removed due to copyright restrictions.
Citation: Figure 10-2. Broecker, W. S., and T. H. Peng. *Tracers in the Sea*. Eldigio Press Lamont Doherty Geological Observatory, 1982, 690 pages.

"Excess CO_2" method: (over) simplified concept



“Anthropogenic” CO_2 E-W section in the North Atlantic

Image removed due to copyright restrictions.

Kortzinger et al. “Anthropogenic CO2 E-W section in the North Atlantic.” *J Geophys Res* 103 (1998): 18,686.

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Modeling the future evolution of anthropogenic CO_2

Image removed due to copyright restrictions.
Citation: Figure 10-14. Broecker, W. S., and T. H. Peng.
Tracers in the Sea. Eldigio Press Lamont Doherty Geological Observatory, 1982, 690 pages.

CO_2 projections for the next 1000 years

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Citation: Figure 1. Caldiera and Kasting. *Nature* 366 (1993): 251-253.

Projection of CO_2 for the next 40,000 years

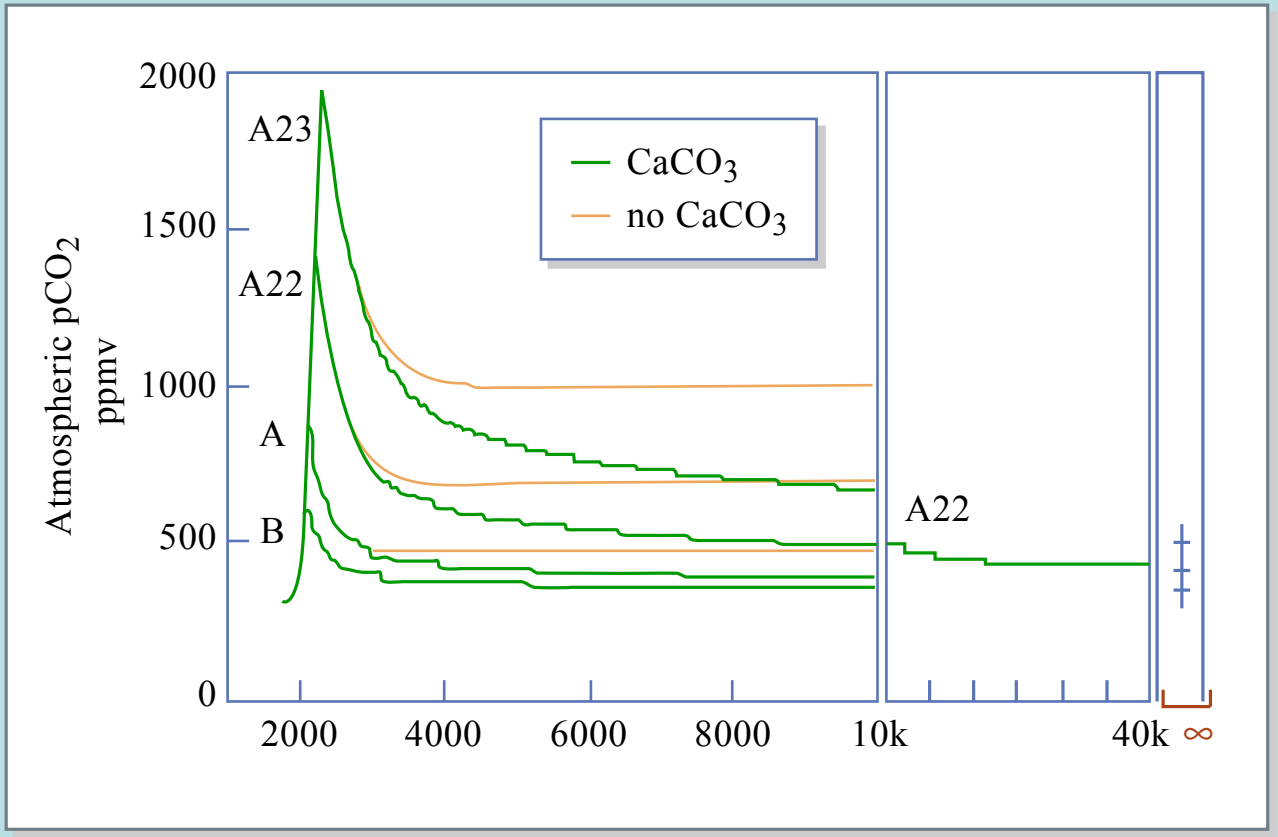

Figure by MIT OpenCourseWare. Adapted from Archer et al., 1997. Similar scenarios have been presented previously by Eric Sundquist.

source: Archer et al. (1996)

Ocean acidification: another consequence of increasing CO_2

- As CO_2 increased from 280 to 375 ppmV in the atmosphere, tropical ocean surface water pH dropped by 0.10 pH unit. When CO_2 is doubled, pH will drop another 0.14 unit.

- This drop in pH decreases the supersaturation of the upper ocean with respect to $CaCO_3$.

- The rate of calcification by corals and other carbonate-secreting organisms decreases as saturation decreases.

Alternatives to continued fossil fuel CO_2 emissions

- **Conservation**
  - One could envision perhaps a factor of two improvement in fuel consumption (hybrid vehicles) and continuing improvements in other energy uses. But it would be extremely difficult for conservation alone to solve the problem.

- **Find other energy sources**
  - Most alternatives have limited potential at the present; future developments may improve their viability:
  - Wind Power: now economically viable to some extent given government subsidy. Problems: NIMBY, requires backup when winds are weak.
  - Solar: Not economically viable now except in remote areas or given government subsidy (California). There is potential for efficiency improvement, but as for wind power, requires backup or storage for night and when overcast.
  - Nuclear: This option is probably the only one that could reliably provide large scale base power. It cannot directly serve transportation, although it could be enlisted as a source of hydrogen or to charge (hypothetical) improved batteries for electric cars. In some regions it is important now (e.g. France). But in other regions safety concerns have made it uneconomic (e.g. U.S.). The safety issue possibly may be overcome, but the large scale introduction of nuclear power would worsen its own environmental problem: what do we do with spent fuel that remains radioactive for tens of thousands of years? There is no demonstrated solution yet, although demonstration projects (e.g. Yucca Mountain) are underway.

- **Carbon sequestration**

  The idea is to capture CO_2 (most efficiently done at the site of fossil fuel consumption) and then place it somewhere where it will not reach the atmosphere for thousands of years.
- Capture is done most efficiently at large power stations; it is difficult to impossible for small or mobile sources.
- Capture can be achieved by several technologies: quaternary amines can retain carbon and the release it; power plants could be fueled by 100% oxygen so that the entire effluent is pure CO_2; and there are other possibilities. But all of these require energy to operate, so we will have to use more fossil fuel in order to capture it – also using up fossil fuel reserves more rapidly.
- Once captured, energy will be require to sequester the CO_2 somewhere.
- One possible reservoir is the deep sea – injection of carbon will eliminate the "lag" of ocean CO_2 uptake, but will leave 20% of emissions in the atmosphere for thousands of years; best thought of as a "peak shaving" device.
- Geological formations are another possible reservoir is; gas and oil have remained trapped in them for 100's of million years, so they can be quite stable. But the knowledge for reliably pumping CO_2 into these reservoirs is not complete, and a lot of geological study and demonstration pilot tests would be necessary before we can rely on containment.

- More speculative solutions: Fe fertilization of Southern Ocean, mirrors in orbit, SO_2 aerosols in stratosphere.

For further reading:

- Sarmiento, J.L. and N. Gruber (2006) Ocean Biogeochemical Dynamics, Princeton University Press, 503 p.