12.842
Climate Physics and Chemistry
Fall 2006

Natural and Fossil Fuel CO$_2$ in the Ocean (II)
Direct measurements of CO$_2$ in the atmosphere for the past 47 years
Atmospheric CO₂ growth rate

Going up. Annual global rates of CO₂ accumulation in the atmosphere and CO₂ emission from fossil fuel burning since 1958 (2).
Fossil fuel CO$_2$ absorption by the ocean: how much, how fast?

How fast does the ocean absorb CO$_2$? What are the important rate- and capacity-limiting processes? How might these processes change in the future?

- **Direct observation of changing ocean CO$_2$ concentrations** ("the oceanic Keeling Curve"): this method is difficult because the ocean response is 10% of the atmospheric forcing. The CO$_2$ content of the atmosphere has increased by 20% over the past 45 years, so ocean water in equilibrium with the atmosphere has only increased by 2%. And most of the absorbed CO$_2$ has been mixed into a large pre-existing background in the deep ocean, so the signal is much less than 2%.

- **Estimation by subtracting out the natural background**, based on "Redfield Ratio" stoichiometry. This method relies on the higher accuracy of recent measurements and the stoichiometry of the oxidation of marine organic matter. Works reasonably well for North Atlantic, more difficult for Southern Ocean and Pacific (higher background, less certain initial conditions).

- **Tracer method, combined with simple robust models**: tracers such as bomb tritium and chlorofluorocarbons enter the ocean from the atmosphere, much as does CO$_2$. We can safely assume that water that has tritium and CFCs also has anthropogenic CO$_2$. The method requires some correction for the chemical differences between these tracers and for the different time histories of emissions. Nonetheless, these corrections are straightforward and the model-dependence is not strong.
Change of $pCO_2$ at the ocean surface at the JGOFS station HOT over the 13 years period, 1989 - 2002

D. Karl, JGOFS Ocean Science Conference
Washington DC, May 2003
Global Carbon Fluxes

The diagram illustrates the carbon cycle, showing the exchange of carbon between the atmosphere and various reservoirs. The numbers indicate the approximate annual fluxes of carbon (in the form of carbon dioxide) and the approximate amount stored in each reservoir in billions of metric tons. The existing cycles—on land and the other in the oceans—remove about as much carbon from the atmosphere as they add, but human activity (deforestation and fossil-fuel burning) is currently increasing atmospheric carbon by some three billion metric tons yearly. The numbers are based on work by Bert Bolin of the University of Stockholm.

Units: gigatons of C
(per year for fluxes)
The Revelle Factor

Revelle Factor\[ R = \frac{\Delta p_{\text{CO}_2}}{\Delta \Sigma \text{CO}_2} \frac{p_{\text{CO}_2}}{\Sigma \text{CO}_2} \approx 10 \]

\[
\begin{align*}
\text{CO}_2 (\text{gas}) \quad \uparrow & \quad \downarrow \\
\text{CO}_2 (\text{dissolved}) \quad \Leftrightarrow & \quad H^+ + HCO_3^- \quad (85.7\%)
\end{align*}
\]

\[
\begin{align*}
H^+ + CO_3^- \quad (13.9\%)
\end{align*}
\]
Ocean uptake of fossil fuel CO$_2$: two limiting cases and the real situation
Fundamental factors controlling ocean fossil fuel CO$_2$ uptake

• Physical transfers:
  – CO$_2$ crosses the air-sea interface
    - Chemical equilibrium determines total possible transfer
      (carbonic acid equilibrium constants, summarized by Revelle Factor)
    - Gas exchange dynamics across the air-sea interface determines the rate of approach to chemical equilibrium. Gas exchange is a function of wind speed and other factors.
      - Estimated from bomb $^{14}$C uptake and $^{222}$Rn deficit
  – CO$_2$ that dissolves into the surface mixed layer is carried by ocean circulation into the upper ocean and deep sea.
    • How fast does this occur, and what factors affect the rate of circulation?
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 CO2 uptake
  - $\delta^{13}$C
  - “excess CO$_2$”
  - Historical proxy methods: $\delta^{13}$C in tree rings and corals
- Extrapolating fossil fuel into the future
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Figure 3-2. Gas exchange model. A thin film of "stagnant" water separates the well mixed overlying air from the well mixed underlying surface water. Gases are transferred between air and water only by molecular diffusion through this film. The concentration of gas within the film grades from that corresponding to equilibrium with the overlying air at the top to that found in the surface ocean at the base. The film thickness decreases as the degree of agitation of the interface increases. In the ocean, this film averages about 40 microns in thickness (a micron is one-millionth of a meter).


 Flux = D \frac{c_m - c_0}{z_{film}}

where 
- $c_m$ = concentration of dissolved gas in (interior) mixed layer of ocean
- $c_0$ = concentration of dissolved gas at surface of ocean (equilibrium with atm)
- $z_{film}$ = thickness of stagnant film
- $D$ = diffusion coefficient of dissolved gas
Note: diffusion is random in direction and gas exchange occurs in both directions. A net flux occurs when there is a concentration gradient where there are more atoms going in one direction than in the other.
Piston velocity

- $D/z$ has dimensions of velocity.
- Gas exchange diffusion through the stagnant film acts as if two pistons, moving in opposite directions, are sweeping the dissolved gases in and out of the stagnant film.
- Piston velocity for CO$_2$ in the ocean is about 2000 m/yr.
**222**Rn deficit method for determining gas exchange rates

Figure 3-3. Concentration of radon gas as a function of depth at Atlantic GEOSECS station 57 (24°S 35°W). The concentration expected if no radon were escaping to the atmosphere is shown by the dashed line. The difference between this equilibrium value and the observed value is a measure of the amount of radon lost to the atmosphere. The shaded area is a measure of the total amount of radon lost to the air. From the amount of missing radon it is possible to determine the piston velocity for gas exchange. The dotted line is the temperature profile at this station defining the depth of the wind-stirred layer. These results were obtained as part of the GEOSECS program (175).  

Global average CO$_2$ exchange rate from natural radiocarbon

- $^{14}$C is formed at the top of the atmosphere by the interactions of cosmic rays with atmospheric gases.
- This $^{14}$C is then (well) mixed in the atmosphere and enters the ocean.
- The decay rate of $^{14}$C in the ocean + atmosphere + biosphere $\approx$ ocean is equal to the production rate.
- Hence the flux of $^{14}$C into the surface ocean must be equal to the difference in radiocarbon concentration between the atmosphere and mixed layer of the ocean.
- So we can calculate $z_{\text{film}}$ from natural radiocarbon.
Gas exchange increases with increasing wind speed
Surfactants can also affect gas exchange

Experiments in wind-wave tunnels have demonstrated that surfactants can decrease $k_L$ at a given wind speed compared to the $k_L$ value measured at the same wind speed for transfer through a clean surface [Broecker et al., 1978; Frew et al., 1995]. Figure 4 shows $k_L$ measured by Frew [1997] in a small annular wind-wave flume plotted versus rotor speed (which is the tangential speed of the fan blades driving the circular wind field in the tunnel) for clean water and water containing varying concentrations of surface active material. The plot of $k_L$ versus rotor speed in Figure 4 for the clean water case resembles the quadratic form proposed by Wanninkhof [1992]. In contrast, the data in Figure 4 from the experiments conducted with surfactants are similar to the first two segments of the Liss and Merlivat [1986] relations. Although this bilinear behavior has been observed in earlier wind-wave tunnel experiments [Broecker et al., 1978; Jähne et al., 1984a], Frew [1997] showed that the wind speed where the breakpoint between the two linear segments occurs is a function of surfactant concentration. Frew [1997] conducted experiments using material extracted from the coastal marine surface microlayer and soluble synthetic surfactants, the latter of which do not form films on the water surface. The data in Figure 4 show that $k_L$ can be surfactant influenced even in the absence of a visible coherent film. Finally, the data in Figure 4 and the previous studies of Frew et al. [1990] demonstrate that naturally occurring surfactants can decrease gas transfer rates.

Figure 4. The gas transfer velocity, $k_L$, plotted as a function of rotor speed from the data of Frew [1997] collected in an annular wind tunnel for clean water, natural coastal seawater, and water containing two different concentrations of a synthetic surfactant. Data key is shown on the figure.
Artificial gas exchange experiment

Fig. 6. Survey track during the experiment (dots) and locations where SF₆ concentrations were 10 times greater than background (circles). The tracer was released between 41°22'N, 67°51'W and 41°27'N, 67°47'W. The depth contours are in 18.3-m (10 fathom) intervals.

Fig. 7. Change in $^{3}$He/SF₆ ratio over time. The error bars refer to the standard deviation in the ratio at four depths. The time intervals used for interpretation of the data are indicated by the solid marks on the $X$ axis.

Change in maximum observed SF₆ concentration with time in the patch.
Recent estimates of gas exchange rate as a function of wind speed

Fig. 8. Gas transfer velocities from CO2 direct covariance, CO2 atmospheric profiles, DMS atmospheric profiles, and the dual-tracer techniques. The flux parameterizations of Wanninkhof (1992) (dotted line) and Liss and Merlivat (1986) (dashed line) using the mean ΔpCO2 are shown for comparison. A cubic relationship (solid line) using a non-zero offset is also shown for comparison (McGillis et al., in press).
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 Rate of exchange of CO$_2$ between ocean and atmosphere:

$$2000 \text{ m yr}^{-1} \times 10^{-5} \text{ moles kg}^{-1} \times 1000 \text{ kg m}^{-3} = 20 \text{ moles m}^{-2} \text{ yr}^{-1}$$

Piston velocity  conc. of gaseous dissolved CO$_2$ conversion factor

Exchange rate of CO$_2$ across air/sea interface
Global Carbon Fluxes

Units: gigatons of C (per year for fluxes)
$p_{CO_2}$ varies in surface ocean waters:
some areas take up CO$_2$, others exhale it

Blue = $p_{CO_2} < -30 \mu atm$ rel to atm

Red = $p_{CO_2} > +30 \mu atm$ rel to atm.

Fig. 3. The distribution of $p_{CO_2}$ of the world’s oceans expressed as the departure in ppm from equilibrium with atmospheric CO$_2$. $H$ indicates high; $L$, low.
CO₂ can show strong short-scale variability (e.g. the North Atlantic ocean)
Change of pCO$_2$ at the ocean surface at the JGOFS station HOT over the 13 years period, 1989 - 2002
Mean Annual Flux for 1995 (Wind Speed)$^2$ Wanninkhof (1992)

Net Flux (moles CO$_2$ m$^{-2}$YEAR$^{-1}$)

T. Takahashi LDEO web site
Takahashi CO2 flux estimates by cause
Estimating Ocean of Fossil Fuel CO$_2$ Uptake

- CO$_2$ in the atmosphere equilibrates on a timescale of less than a year. Hence this is not a rate-limiting step (mean life concept).
- 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.
The solubility pump: CO$_2$ is more soluble in cold waters than in warm waters (the thermal pump), and more soluble in fresher waters than saltier waters (the salt pump). If alkalinity were uniform throughout the ocean and if both cold and warm surface waters equilibrated their $p_{CO_2}$ with the atmosphere, then cold surface waters would have a higher dissolved carbon dioxide content than warm surface waters. As these cold surface waters circulate into the deep interior of the ocean, deep waters will have more CO$_2$ than warm surface waters.
Figure 3.2.1: Plot of the solubility of various gases as a function of temperature. The solubility of all gases decreases with increasing temperature, but there exist large differences in the solubility of the different gases for a particular temperature. These differences can be understood in terms of their molecular weight (ideal gas) or other factors, such as molecular interactions between the gas and the water (nonideal gas). Note the change in vertical scale between panels (a) and (b). Based on the empirical functions listed in table 3.2.2.

From Sarmiento and Gruber (2006)
The carbon “biological pump”

- **The biological pump:** organisms remove carbon and nutrient elements from the surface ocean (which is equilibrated with atmospheric oxygen; note oxygen solubility is a function of temperature); the debris from these organisms sinks and decomposes, releasing carbon and nutrient elements into the deep water and consuming oxygen.

  - **classical Redfield Ratio:**

    - \((\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 138 \text{ O}_2 \rightarrow 106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4\)

    - This stoichiometry proposed by Redfield is based on elemental ratios he observed in ocean water samples and plankton. It considers marine organic matter as if it were a mixture of carbohydrates (\(\text{CH}_2\text{O}\)), proteins (containing \(\text{NH}_3\)), and phospholipids and nucleic acids (\(\text{H}_3\text{PO}_4\) bearing). In reality, a broad mixture of compounds occur, and the observed stoichiometry \(\Delta \text{O}_2:\Delta \text{C}\) in deep ocean waters implies a higher value (~165), because of the presence more hydrocarbon-like functional groups:

    - \((\text{CH}_2\text{O})_{111}(\text{CH}_4)_{11}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 165 \text{ O}_2 = 122 \text{ CO}_2 + 16 \text{ HNO}_3 + 149 \text{ H}_2\text{O} + \text{H}_3\text{PO}_4\)

    - Note the production of nitric and phosphoric acid in this process; this acid changes alkalinity. Once you acknowledge this process, you also need to take into account another effect that reduces the acid effect on alkalinity by about \(1/3\): the presence of ion-exchanged carboxyl groups:

      - \((\text{CH}_2\text{O})_{102}(\text{CH}_4)_{14}(\text{HCOO-Na}^+)_6(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 165 \text{ O}_2\)

        - \(\Rightarrow 122 \text{ CO}_2 + 16 \text{ HNO}_3 + 146 \text{ H}_2\text{O} + \text{H}_3\text{PO}_4 + 6 \text{NaOH}\)

    - There is debate on whether the C:P and N:P stoichiometries are fundamental to marine ecosystems, or whether there is some plasticity (e.g., could N:P = 25?). (There is less debate on variable C:N ratios than for C:P).

    - We should also note that some organisms precipitate inorganic shells out of calcium carbonate (\(\text{CaCO}_3\)) and silica (\(\text{SiO}_2\cdot\text{nH}_2\text{O}\)). For example for every 106 organic carbon atoms converted to organic matter, about 22 \(\text{CaCO}_3\) molecules are precipitated (ocean-wide average).
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Ocean Surface Currents: schematic

Figure 3-13  Major features of the surface circulation of the oceans. From McLellan, 1965:opposite p. 42. Reprinted by permission of Pergamon Press and H. McLellan.
Plate 6. (a) Decadal-mean surface velocity field resulting from the quasi-Eulerian averaging of drifter trajectories in 1° square boxes. Vectors are shown only for boxes in which the magnitude of the mean velocity exceeds one standard error. Error ellipses correspond to one standard error in the zonal and meridional directions. Red yellow vectors indicate velocity magnitudes greater than 30 and 15 cm s$^{-1}$, respectively. (b) A schematic diagram representing the most significant surface circulation features identified in the drifter-derived mean velocity field. For clarity, several features are abbreviated as follows: Gulf of Mexico Loop Current (LC), Caribbean Current (CC), Fram Strait Current (IC), Norwegian Current (NC), East and West Greenland Currents (EGC and WGC). Eddy kinetic energy (EKE), defined as one-half the sum of the zonal and meridional velocity variances, results from 1° quasi-Eulerian averaging of the drifter trajectories.
The “eddy revolution”
• 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)
Western North Atlantic Potential Temperature Section
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 ($^3$H) 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

Data of Ostlund (U. Miami)

1972

1981
CFC 11 in the North Atlantic Ocean

DONEY SC, BULLISTER JL
A CHLOROFLUOROCARBON SECTION IN THE EASTERN NORTH-ATLANTIC
DEEP-SEA RES 39:1857-1883, 1992
CCl₄ zonal section in the South Atlantic (11.7°S)

Distribution of CCl₄ (pmol/kg) on A8, see Fig. 6.

Source: Roether and Putzka (1996)
CFC 11 Atlantic Ocean Meridional Section
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

Raynaud et al., 2000
QSR Vol. 19, No's 1-5
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 \( F(t) = \text{CO}_2 \) emissions

The mean age of CO$_2$ at present is about 28 years
### Table 1. IPCC global CO$_2$ budget for 1980–1989 [as adapted from (38) by (56)].

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Average flux (Gt of C year$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sources</strong></td>
<td></td>
</tr>
<tr>
<td>Fossil fuels</td>
<td>5.4 ± 0.5</td>
</tr>
<tr>
<td>Deforestation and land use</td>
<td>1.6 ± 1.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>7.0 ± 1.2</td>
</tr>
<tr>
<td><strong>Sinks</strong></td>
<td></td>
</tr>
<tr>
<td>Atmosphere</td>
<td>3.2 ± 0.1</td>
</tr>
<tr>
<td>Oceans (modeled uptake)</td>
<td>2.0 ± 0.8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>5.2 ± 0.8</td>
</tr>
<tr>
<td>Imbalance (sources – sinks)</td>
<td>1.8 ± 1.4</td>
</tr>
</tbody>
</table>
Other ways to estimate ocean CO$_2$ uptake

- CO$_2$ influx/efflux estimate (from $\Delta p_{CO_2}$)
- Loss of oxygen from the atmosphere
- $\delta^{13}C$ of oceanic CO$_2$ (because fossil fuels are $\sim -27\%o$ compared to $\sim 0\%o$ for the ocean) O$_2$ influx/efflux estimate (from $\Delta p_{CO_2}$)
- “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. Data from additional sites in the Scripps $O_2/N_2$ network (not shown) indicate that the interannual trends and north-south gradients inferred from these three sites are characteristic of large-scale atmospheric patterns.
Vector diagram showing the calculation of the global land biotic and oceanic carbon sinks. Solid circles are annual averages of the observed O₂ and CO₂ concentrations, calculated from global averages of Alert, La Jolla, and Cape Grim. Also shown is a fossil fuel combustion line, representing the change in atmospheric O₂ and CO₂ concentrations that would have occurred if all CO₂ emitted remained in the atmosphere. The slope for the land biotic sink is fixed to an O₂:C molar ratio of −1.1, the best estimate of the ratio observed for land photosynthesis and respiration processes, whereas the oceanic sink assumes that there is no effect on O₂, as described in the text.

Source: R. Keeling lab
Another O$_2$-CO$_2$ time series

Fig. 1. The $\delta$O$_2$/N$_2$ and CO$_2$ records measured (18) in air collected at six sites (35). Axes have been scaled so that removals of 1 mol each of O$_2$ and CO$_2$ result in the same displacement. The secular trend in $\delta$O$_2$/N$_2$ is primarily due to combustion of fossil fuel. The seasonal cycle of $\delta$O$_2$/N$_2$ has a terrestrial component that is the inverse of the CO$_2$ variation times the photosynthetic stoichiometry (1.1) (17). The oceanic contribution to the seasonal $\delta$O$_2$/N$_2$ variation reflects photosynthesis and ventilation as discussed in the text. There is also a thermal component to the cycle driven by changes in the sea surface temperature and the different solubilities of O$_2$ and N$_2$ (7). Also shown are adjusted values (18) of previously published SIO data of Keeling et al. (15) for Alert and Cape Grim (35) with respect to GF1 (a flask of standard air of arbitrary composition (8)).
Using $\Delta^{13}$C and carbon isotopes to estimate fossil fuel $\text{CO}_2$ uptake.

**Fig. 4.** Two-year smoothed trends in terrestrial and oceanic carbon uptake based on $\Delta^{13}$C and $\Delta^{13}$C. The light lines show the “global” average of $f_{\text{land}}$ (upper portion) and $f_{\text{ocean}}$ (lower portion). The meaning of “global” changes as records from new stations are added to the average. Dark lines show the global average values for land and ocean carbon storage based on the NOAA-CMDL/CU-INSTAAR $\Delta^{13}$C data set (11) adjusted to the CSIRO calibration, as described in the text. Carbon fluxes and global average values are calculated from the $\Delta^{13}$C measurements according to the methods of Ciais et al. (9). $G$ has been adjusted to 83.6 GtC %0/year to optimize $\Delta^{13}$C-$\text{O}_2$ agreement for the 6-year average fluxes (Fig. 3). $\text{O}_2$-based records have been calculated as if each station represented the entire atmosphere.

Battle, Bender, Tans et al. (2000) Science 287:2467
CO₂ uptake by leaves

Cross-sectional view of a typical plant leaf, showing the upper (palisade) layer of cells, in which photosynthesis occurs, and the guard cells, which control the diffusion of CO₂ (in) and H₂O and O₂ (out) through stomates on the lower surface. A summary of the photosynthetic reaction occurring in the chloroplasts of the palisade cells is shown in the insert.

source:
Schlesinger,
Biogeochemistry
Increasing amplitude and length of the growing season

FIG. 1 Trends in relative amplitude and timing of the seasonal cycle of atmospheric CO₂. a, At Mauna Loa Observatory, Hawaii. Annual values of the amplitude (upper plot, dots connected by dashed lines) were determined from weekly averaged continuous concentration data 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, 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 (solid curve, with standard error, σₐ, of 0.028%) shows quasi-decadal changes in the relative amplitude. The timing of the downward zero crossing of the seasonal cycle (lower plot, dots connected by solid line segments), was obtained from 3-year fits to the CO₂ record, as described in the text and plotted relative to the 212th day of the year. The zero crossing is with respect to the seasonally adjusted CO₂ concentration determined by the method of ref. 3. b, As a, but...
Deforestation in the United States

**Disappearing Forests**

Before the arrival of European settlers, a vast expanse of forest covered much of the country. As development has proceeded, all but a few pockets of virgin forest have been destroyed. Some forests are recovering but remain biologically impoverished.

**Extent of virgin forest**

- In 1620
- In 1850
- Striped areas indicate scattered pockets
- In 1990

Sources: National Geographic, 1990; Atlas of the Historical Geography of the United States, 1932; Wilderness Society

The New York Times
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Atmospheric $\delta^{13}C$ of CO$_2$, 1976-1995

**Figure 13.** Atmospheric $\delta^{13}C$ measurements at Mauna Loa, Hawaii, and the south pole. The curve is a prediction from the box diffusion model describe in the text with a diffusivity $K$ of 4000 m$^2$ yr$^{-1}$ and variation of surface water temperature according to data of Jones et al. [1986a, 1986b, and personal communication, 1994].
Temperature-dependent carbon isotope equilibration with the ocean: now and pre-anthropogenic

Figure 10-22. Diagrammatic representation of the relationship between the δ¹³C for surface water carbon and temperature as measured in 1973 (see figure 6-12 for data) and the δ¹³C which surface water carbon would have had were it at equilibrium with the 1973 atmosphere (δ¹³C = -7.2‰). Also shown are the surface water δ¹³C averages reconstructed for the period before the impacts of man (the combined forest-soil and the fossil fuel CO₂ input yielded a drop of 0.95‰ in the model's surface ocean between 1850 and 1973). Finally, the δ¹³C values for ocean water at equilibrium with the pre-1850 atmosphere (δ¹³C = -5.6‰) is shown. The 1.6‰ decrease in δ¹³C for atmospheric CO₂ between 1850 and 1973 is that obtained from the model. While individual areas of the ocean were not at isotope equilibrium with the air the sea surface as a whole must have been at steady state prior to the year 1800.
Changing $\delta^{13}C$ of the ocean due to fossil fuel uptake

Fig. 1. The location of the cruise tracks for the HUDSON-70 cruise in May 1970 (solid diamonds) and the three NOAA cruises in February and March 1989 (circles), March and April 1990 (squares), and March and April 1991 (triangles).

Fig. 2. The decrease of the $\delta^{13}C$ values of dissolved inorganic carbon in the mixed layer of the Pacific Ocean since 1970. Symbols correspond to those in Fig. 1.

Source: Paul Quay
Evolving Pacific Ocean $\delta^{13}C$ depth profiles

**Fig. 3.** The change in the depth distribution of the $\delta^{13}C$ of the dissolved inorganic carbon since 1970 in the Pacific Ocean. The station comparison at 0°N uses $\delta^{13}C$ measurements on samples collected in September 1991 at Station 262 of the WOCE P16C cruise. The uncertainty of the measurements is approximately ±0.04 per mil for the 1970 data and ±0.02 per mil for the 1989 to 1991 data.

*Source: Paul Quay*
Using ice core CO₂ and tree-ring δ¹³C data to estimate anthropogenic carbon emissions.

Figure 10-2. A scenario (based on the tree-ring-based atmospheric ¹³C/¹²C record) for the net release of CO₂ from the forests and soils over the last 200 years. Also shown is the documented record of fossil fuel CO₂ release. The total production from these two sources is also given.
“Excess CO$_2$” method: (over) simplified concept

\[
\begin{align*}
\text{TCO}_2 & \quad \text{excess anthropogenic CO}_2 \\
\text{P} & \quad \text{natural CO}_2\text{-P (Redfield Ratio)}
\end{align*}
\]
“Anthropogenic” CO$_2$ E-W section in the North Atlantic
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 ΔO$_2$/ΔCO$_2$ method for estimating ocean and biospheric fossil fuel uptake: quantifying the “missing sink”
- Other methods for observing fossil fuel CO$_2$ uptake
  - δ$^{13}$C
  - “excess CO$_2$”
  - Historical proxy methods: δ$^{13}$C in tree rings and corals
- **Extrapolating fossil fuel into the future**
Figure 10-14. Multibox ocean model used to calculate the uptake of fossil fuel CO$_2$ by the ocean. The ocean is divided into 76 layers each with the same volume. Water is traded between adjacent reservoirs (equivalent to vertical eddy diffusion). Water also passes up from the bottom of the model to the level designated as the source for new deep water. From here it is transferred to the polar outcrop where it is cooled without undergoing modification in its ECO$_2$ content and carbon isotope ratios. This water is then transferred to the model's bottom box. The PO$_4$ reaching the uppermost reservoir is entirely utilized by plants. These plants are assumed to incorporate 105 carbon atoms for each phosphorus atom. The organic matter so produced falls toward the bottom. As it falls it is progressively oxidized returning the carbon and phosphorus to solution.

Broecker and Peng, 1984
1. Logistic 4.3% yr\(^{-1}\)
2. Logistic 2.35% yr\(^{-1}\)
3. Stabilize at 750 p.p.m.
4. Stabilize at 550 p.p.m.
5. Stabilize at 350 p.p.m.

**FIG. 1 a, Atmospheric CO\(_2\) scenarios for which non-steady-state impulse–response functions were calculated. b, Total fossil fuel plus net biosphere CO\(_2\) emissions calculated by the box-diffusion model, corresponding to each of these atmospheric CO\(_2\) scenarios.**

The logistic growth equation used to describe scenarios 1 and 2 is \(\frac{dQ}{dt} = \mu Q(1 - Q/R)\) where \(dQ/dt\) is the CO\(_2\) emission rate, \(R\) is the total recoverable fossil fuel (5,000 GtC), \(\mu = 4.3\) and 2.35% for scenarios 1 and 2, respectively. \(Q\) was adjusted such that emissions were 6 GtC yr\(^{-1}\) in 1990. For scenario 5, net emissions must be \(<0\) near year 2100 to stabilize atmospheric pCO\(_2\) at 350 p.p.m. This could occur if fossil fuel burning were greatly reduced and the biosphere acted as a net sink for CO\(_2\).
Projection of CO$_2$ for the next 40,000 years

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\textsubscript{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\textsubscript{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\textsubscript{2} somewhere.
  • One possible reservoir is the deep sea – injection of carbon will eliminate the “lag” of ocean CO\textsubscript{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\textsubscript{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\textsubscript{2} aerosols in stratosphere.
Vertical chemical profiles in the ocean


**Figure 1-1.** Plots of temperature, salinity, dissolved oxygen content and nitrate content as a function of water depth at GEOSecs station 214 in the North Pacific (32°N, 176°W). Potential temperature rather than the temperature measured in situ is given. The salinity profile in this region of the ocean shows a pronounced minimum at a depth just over 600 meters. This intermediate water (as it is called) forms in the northern Pacific and sinks and flows laterally beneath the waters of the warm temperate ocean. The level of this minimum is shown in the other diagrams by a dashed line. Dissolved oxygen is utilized by animals and bacteria living in the deep sea to "burn" the organic debris falling from the surface. Thus all deep waters are deficient in oxygen compared to the amount they received from the atmosphere before descent. As oxygen is consumed, nitrate is produced. Thus the shapes of the profiles of these two properties have an inverse relationship. These results were obtained as part of the GEOSecs program (425). The location of this station can be seen on the foldout map.

**Figure 1-2.** Plots of total dissolved inorganic carbon, alkalinity, dissolved silicate, and dissolved barium as a function of water depth at GEOSecs station 214 in the North Pacific (32°N, 176°W). As in figure 1-1 the dashed line represents the depth of the salinity minimum. The alkalinity of the sea changes mainly because Ca is extracted from surface waters by organisms to form CaCO₃ skeletal material. Much of this CaCO₃ dissolves after falling to the deep sea. The depth profiles of these constituents differ from one another and from that of nitrate because they are carried down in different forms; C and N in organic debris, C and Ca in CaCO₃, Si in opaline silica, and Ba in some as yet unidentified form. The depth spectrum of the destruction of these various phases is not the same. The skeletal matter reaches, on the average, greater depths before dissolving than the organic debris reaches before consumption. This gives rise to deeper maxima for alkalinity, silicate and barium than for nitrate and carbon. These results were obtained as part of the GEOSecs program (425).