1 Short-term evolution of atmospheric CO_2

We have spoken of volcanism as the *long-term* source of CO_2.

Among the other sources, the respiration flux is about 3 orders of magnitude greater than volcanism, and fossil-fuel combustion is about one and one-half orders of magnitude greater.

Whatever the source, we consider the following questions:

- How can we identify the source?
- How long does CO_2 stay in the atmosphere?

We shall answer these questions in a precise way that pertains to short, roughly decadal, time scales.

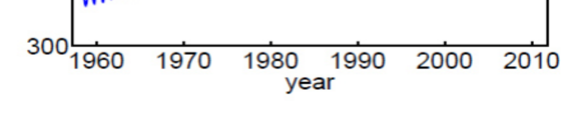
We first consider the growth of atmospheric CO_2 since the mid-20th century.

1.1 The Keeling curve

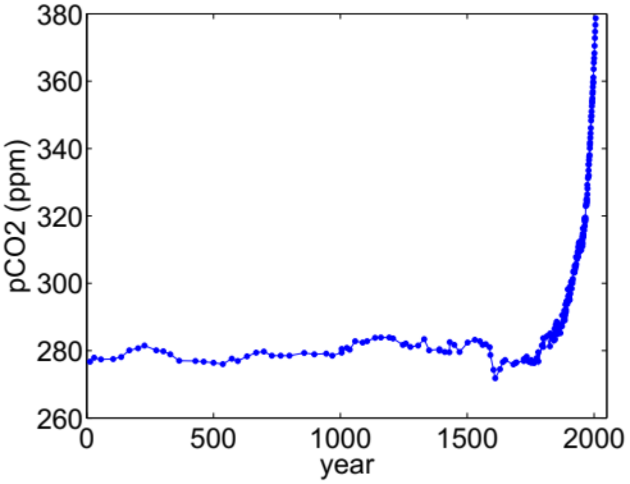
Atmospheric CO_2 concentrations have been measured monthly at Mauna Loa Observatory, Hawaii, since 1958.

The measurements, begun by C. David Keeling, report CO_2 concentration as a dry mole fraction: the number of molecules of carbon dioxide divided by the number of molecules of dry air multiplied by one million (ppm).

The resulting plot is known as the *Keeling curve*:



Studies of CO_2 in ice cores show that this increase is the latest chapter in process that started about 200 years ago:



Data from the Law Dome ice core, Antarctica [1].

An obvious question arises: Why is CO_2 increasing?

To provide a precise answer, we first digress to a discussion of carbon isotopes.

1.2 Carbon isotopes

1.2.1 Natural abundance

Every atom of carbon has $Z = 6$ protons. Z is the *atomic number*.

When there is no net charge, each atom of C has 6 electrons.

However the *mass number* A varies:

$$A = 12,\ 13,\ \text{or}\ 14.$$

The variation in mass number derives from the variations in the *neutron number*

$$N = A - Z.$$

Each *isotope* of carbon corresponds to a specific neutron number N, and therefore mass number A. These are named according to their mass number:

carbon-12, carbon-13, carbon-14,

and are generally written symbolically as

$$^{12}\mathrm{C}, \quad ^{13}\mathrm{C}, \quad ^{14}\mathrm{C}.$$

^{14}C is radioactive, and ^{12}C and ^{13}C are stable.

About 98.9% of Earth's carbon is ^{12}C and nearly all the rest is ^{13}C; thus

$$\frac{^{13}\mathrm{C}}{\mathrm{C}} \sim 10^{-2},$$

where the denominator represents the sum of all carbon. ^{14}C is much less abundant:

$$\frac{^{14}\mathrm{C}}{\mathrm{C}} \lesssim 10^{-12}.$$

^{14}C is naturally produced in the upper atmosphere by cosmic rays, which can shatter a nucleus (N or O), releasing neutrons, some of which are absorbed by ^{14}N such that

$$^{14}_{7}\mathrm{N} + \mathrm{n}^0 \to ^{14}_{6}\mathrm{C} + \mathrm{p}^+ + \mathrm{e}^-.$$

Thus ^{14}N is converted to ^{14}C, releasing a proton and an electron.

1.2.2 Radioactive decay

^{14}C, being unstable, converts back to ^{14}N.

To understand the rate at which such radioactive decay occurs, we consider briefly the following general model.

Consider the reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{Products},$$

signifying the disappearance or extinction of A with rate constant k.

The meaning of the rate constant k is that, in a small interval of time $\Delta t \ll k^{-1}$,

$$\text{Probability(an arbitrary atom decays)} \simeq k\Delta t.$$

This probability applies to each atom independently, meaning that, whatever the quantity of A, a fraction $k\Delta t$ of A reacts in an interval Δt.

Thus if we have N atoms of A at time t, after a small time Δt, we have

$$N(t+\Delta t) = N(t) - k\Delta t\, N(t)$$

and therefore

$$\frac{N(t+\Delta t) - N(t)}{\Delta t} = -kN.$$

Letting $\Delta t \to \mathrm{d}t$, we have the *first-order decay*

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -kN$$

with solution

$$N(t) = N(0)e^{-kt}.$$

The above development essentially defines a first-order decay process.

Its application to radioactive decay requires merely the assumption that each atom decays with the same constant probability.

For ^{14}C, the rate constant

$$k = \frac{1}{8267\ \mathrm{yr}}.$$

The *half-life* $t_{1/2}$ is the time it takes for one-half of A to decay. Thus

$$\frac{1}{2} = e^{-kt_{1/2}} \quad \Rightarrow \quad t_{1/2} = \frac{\ln 2}{k}$$

For ^{14}C,

$$t_{1/2} = 5730\ \mathrm{yr}.$$

1.2.3 Notation

Geochemists use a very special notation for isotopic abundance.

The first component of the notation is the abundance ratio

$$R_n = \left(\frac{^{n}\mathrm{C}}{^{12}\mathrm{C}}\right)$$

where $n = 13$ or 14.

Geochemists then compare the R obtained on a given sample to R obtained for a "standard" sample. Noting the latter ratio as R_{std}, they define the *isotopic composition*

$$\delta^n\text{C} = \left(\frac{R_n - R_{\text{std}}}{R_{\text{std}}}\right) \times 1000.$$

The factor of 1000 is included because the factor in parentheses is often of order 10^{-2}–10^{-3}, so that when multiplied by 1000 it becomes of order 1–10. One then speaks of δ in units of "per mil", which is equivalent to "parts per thousand," and is written with the symbol ‰, not to be confused with the per cent sign % (parts per hundred).

Analyses of ^{14}C contain even greater notational complexity.

The problem arises from the frequent desire to compare a particular measurement of δ^{14}C (say, of atmospheric CO_2), to the value of δ^{14}C that would be obtained in the absence of anthropogenic perturbation.

Consequently geochemists define the following "cap delta" notation:

$$\Delta^{14}\text{C} = \delta^{14}\text{C} - \left(\delta^{14}\text{C}\right)_0$$

The second term on the RHS is too complicated to discuss here, but it has the property that if δ^{14}C is measured from wood formed in 1850, then $\Delta^{14}\text{C} = 0$.

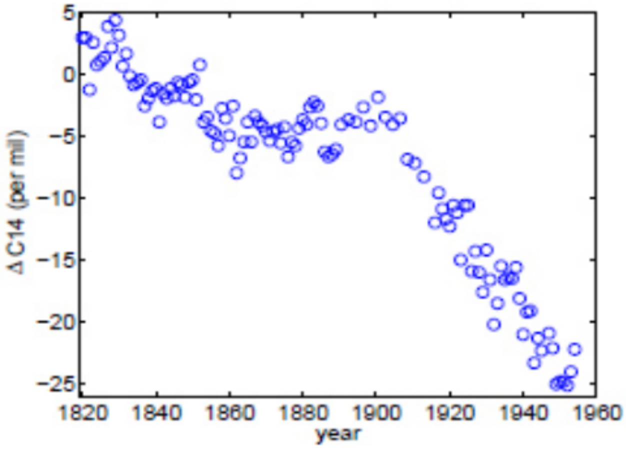
The point is that $\Delta^{14}\text{C} = 0$ represents a "typical" value that represents a balance between atmospheric ^{14}C production and decay.

1.3 The origin of the recent CO_2 rise

CO_2 levels undergo natural fluctuations. Thus it is appropriate to ask whether the recent rise in CO_2 levels are the result of natural changes rather than the burning of fossil fuels.

We can use the ^{14}C content of the atmosphere to help answer this question.

The figure below shows the ^{14}C composition of tree rings associated with the period 1820–1954 [3].



Over the last 50 years, Δ^{14}C decreases by about 20‰.

Over such a time period, natural variations in the cosmic ray flux should produce changes no greater than that of experimental error (a few per mil).

The combustion of fossil fuels, on the other hand, should create such a decrease, because the fuels, being derived from geologically ancient organic matter, are entirely free of ^{14}C.

Thus the ^{14}C content of the atmosphere is diluted by the burning of fossil fuels, so that Δ^{14}C declines.

This phenomenon, known as the *Suess effect*, is one way to trace the source of the recent CO_2 rise to human activities.

1.4 The bomb spike

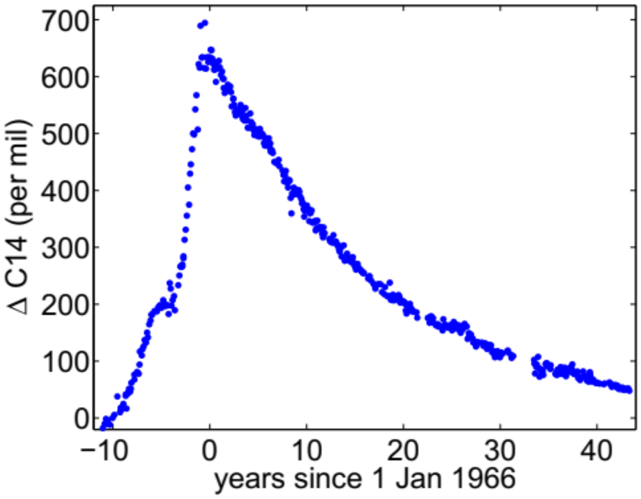
^{14}C can also be used to address the short-term residence time of atmospheric CO_2.

Nuclear weapons tests in the 1950s and early 1960s produced large amounts of ^{14}C in the atmosphere.

The tests were essentially ended by the Nuclear Test Ban Treaty in October

1963.

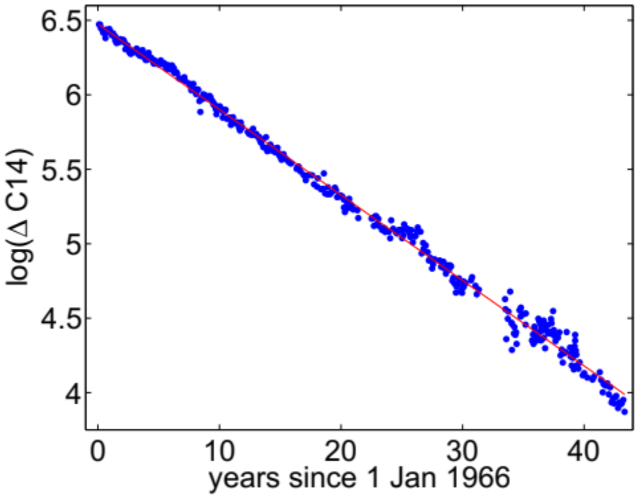
Measurements of atmospheric ^{14}C show the build-up followed by a decay [4]:



The decrease is far too fast to be associated with radioactive decay.

A log-linear plot shows that the decay is nevertheless exponential, dropping off like

$$e^{-t/\tau}, \qquad \tau \simeq 17.4 \text{ yr}.$$



The decay is mostly due to "uptake" of ^{14}C in the oceans, in large part by diffusion.

1.5 Microscopic model of molecular diffusion

To gain some physical insight, we first consider a microscopic model of diffusion.

1.5.1 One-dimensional random walk

Consider a (drunkard's) random walk along a line:

- Start at time $t = 0$ and position $x = 0$.
- Every τ seconds, take a random step s to the left or right.
- Assume equiprobable steps of equal size δ:

$$P(s = \delta) = P(s = -\delta) = 1/2.$$

- No memory (statistically independent jumps).

We think of this as a caricature of real diffusion (e.g., Brownian motion).

Now consider an ensemble of N independent random walks (i.e., many such drunkards, each acting with no awareness of the others).

Let $x_i(n)$ be the position of the ith walker after n steps. Then

$$x_i(n) = x_i(n-1) + s.$$

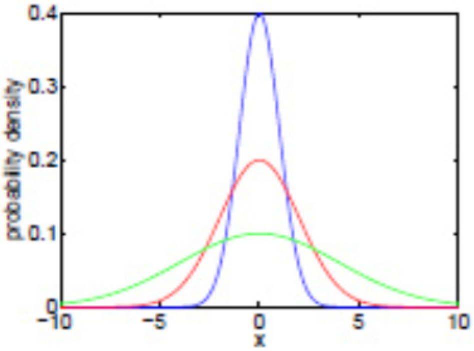
The mean position of a large ensemble of walkers after n steps is

$$\begin{aligned}
\langle x(n) \rangle &= \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} \big(x_i(n-1) + s \big) \\
&= \langle x(n-1) \rangle + \langle s \rangle \\
&= \langle x(n-1) \rangle.
\end{aligned}$$

Here we have used the angle brackets $\langle \cdot \rangle$ to denote the ensemble average. The result shows that the mean position is independent of n, thus retaining permanent memory of the initial condition:

$$\langle x(n) \rangle = 0.$$

Intuitively we understand that there should nevertheless be a wide spread in the probability $P(x)$ that increases with time:



We characterize this spread by the *root-mean-square displacement* $\left\langle x^2(n) \right\rangle^{1/2}$. To calculate it, first write

$$\begin{aligned} x_i^2(n) &= \left[x_i(n-1) + s\right]^2 \\ &= x_i^2(n-1) + 2sx_i(n-1) + s^2. \end{aligned}$$

Because the mean of a sum of random variables is the sum of the means, the mean-square displacement in the ensemble is

$$\begin{aligned} \left\langle x^2(n) \right\rangle &= \left\langle x^2(n-1) \right\rangle + 2\left\langle s\,x(n-1) \right\rangle + \left\langle s^2 \right\rangle \\ &= \left\langle x^2(n-1) \right\rangle + 2\langle s \rangle \left\langle x(n-1) \right\rangle + \left\langle s^2 \right\rangle \\ &= \left\langle x^2(n-1) \right\rangle + \delta^2. \end{aligned}$$

In the second relation, we have replaced the average of a product with the product of averages because s is uncorrelated to x. (This also may be deduced from the observation that the walk contains no memory of past steps.)

Note that our result is in the form of a recursion, which is readily put in the simpler form

$$\left\langle x^2(n) \right\rangle = n\delta^2$$

Since $t = n\tau$, we have

$$\langle x^2 \rangle = \delta^2 t/\tau = 2Dt,$$

where we have defined the *diffusion coefficient*

$$D = \frac{\delta^2}{2\tau}.$$

Thus the mean-squared displacement increases linearly with time, like $2Dt$. Consequently the root-mean-square displacement increases like the square-root of time:

$$\langle x^2 \rangle^{1/2} = (2Dt)^{1/2}.$$

Intuitively we understand that the width of a bell-shaped distribution $P(x,t)$ increases like $\sqrt{2Dt}$.

Indeed, in the plot above,

$$\langle x^2 \rangle^{1/2} = 1,\ 2,\ \text{and}\ 4$$

corresponding to times t such that

$$2Dt = 1,\ 4,\ \text{and}\ 16.$$

For a small molecule in water, $D \simeq 10^{-5}$ cm^2/s. So imagine you're a bacterium (size $\sim 10^{-4}$ cm), and you want to know how long some molecular nutrient will take to diffuse a distance ℓ away from you. Identifying ℓ with $\langle x^2 \rangle^{1/2}$, the diffusion time τ_d is

$$\tau_d \sim \ell^2/2D.$$

Consider two particular cases:

ℓ (cm)	τ_d (s)
10^{-4}	5×10^{-4}
1	5×10^{4}

In other words, the molecule would stay within a length commensurate to a bug's size for only about a millisecond. But it would stay within 1 cm for about 14 hours!

This huge change is a consequence of the quadratic scaling $\tau_d \propto \ell^2$, a hallmark of diffusive processes.

In contrast, for a simple advective flow times scale linearly with distance.

1.5.2 Higher dimensions

Before moving on, we first argue that our little toy problem is equally valid in higher dimensions.

In, say, two dimensions, the random walker is on a plane. In our discrete approximation, this corresponds to a lattice with a "Manhattan metric," with the drunkard originating at his corner bar and moving $\pm\delta$ in each dimension at each time step.

Because the drunk's motion in x is independent of his motion in y,

$$\left\langle x^2 \right\rangle = \left\langle y^2 \right\rangle = 2Dt$$

Since the mean-square distance from the origin is

$$r^2 = x^2 + y^2,$$

we have

$$\left\langle r^2 \right\rangle = 4Dt.$$

The generalization to higher dimensions is obvious. The point is that we retain the diffusive scaling $\ell^2 \propto t$.