

Carbon Cycle Processes

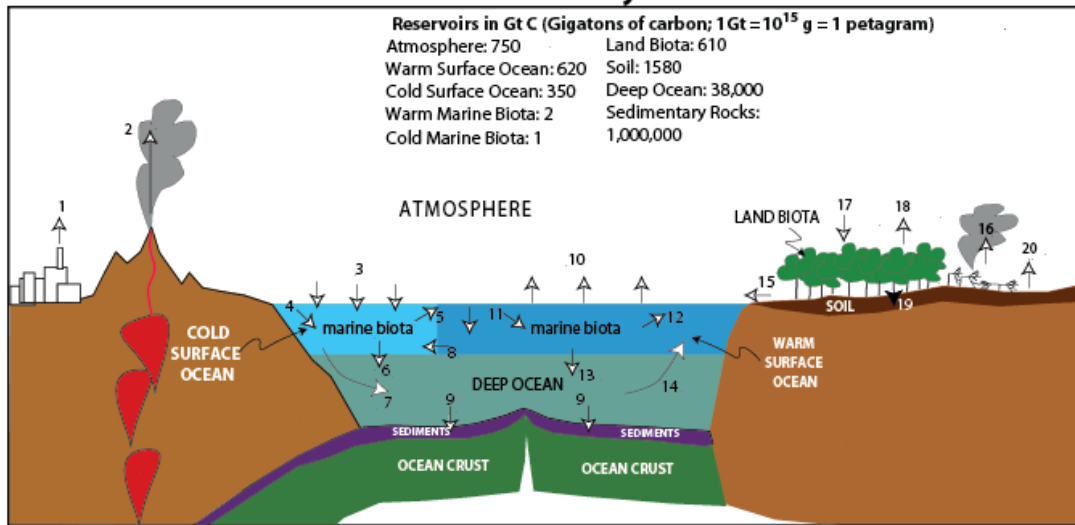
An overview of processes depicted in a STELLA model of the global carbon cycle.

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The Global Carbon Cycle



The global carbon cycle, as best estimated, in 1994. Data slightly modified from Siegenthaler and Sarmiento, 1995; Kwon and Schnoor, 1995.

Key to Flows:

- | | |
|--|---|
| 1) Fossil Fuel Burning — 5 Gt C/yr | 11) Photosynthesis of marine biota in warm surface waters — 32 GtC/yr |
| 2) Volcanic Emissions — 0.6 Gt C/yr | 12) Respiration of living marine biota and rapid recycling of dead biota in warm surface waters — 26 GtC/yr |
| 3) Uptake of CO ₂ by cold surface waters of the oceans — 90 GtC/yr | 13) Sinking of dead marine biota (both organic and inorganic carbon) from warm water into deep water — 6 GtC/yr |
| 4) Photosynthesis of marine biota in cold surface waters — 18 GtC/yr | 14) Upwelling of deep water (at equator and along edges of continents) — 105.6 GtC/yr |
| 5) Respiration of living marine biota and rapid recycling of dead biota in cold surface waters — 14 GtC/yr | 15) River runoff transfers carbon from the land to the sea — 0.6 Gt C/yr (2/3 to warm ocean, 1/3 cold) |
| 6) Sinking of dead marine biota (both organic and inorganic carbon) from cold water into deep water — 4 GtC/yr | 16) Deforestation and land clearing releases CO ₂ into the atmosphere — 1.5 Gt C/yr |
| 7) Downwelling of cold surface water (mainly near the poles) — 96.2 GtC/yr | 17) Photosynthesis of land biota — 110 Gt C/yr |
| 8) Advection (horizontal transfer) from warm to cold surface water — 10 Gt C/yr | 18) Respiration of land biota — 50 Gt C/yr |
| 9) Sedimentation on sea floor (both organic and inorganic carbon) stores carbon in sedimentary rocks — 0.6 Gt C/yr | 19) Litter fall and below-ground loss from plant roots transfers carbon to the soil — 60 Gt C/yr |
| 10) Release of CO ₂ by warm surface waters of the oceans — 90 GtC/yr | 20) Respiration of microorganisms in the soil releases CO ₂ into the atmosphere — 59.4 Gt C/yr |

Processes of Flow in the Terrestrial Realm

Photosynthesis

Plant Respiration

Litter Fall and Below-Ground Addition

Soil Respiration

Runoff

Processes of Flow in the Oceanic Realm

Ocean-Atmosphere Exchange

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Readings and Key References

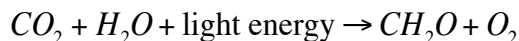
Before we embark on our adventure of modeling the global carbon cycle, it is important to point out that the present-day carbon cycle is not in a steady state. This means that if, as is typical, we want to begin by creating a steady-state model that will serve as our experimental control, we should not force our model to mimic the present day situation. Instead, we will use the carbon cycle in its presumed state just before the onset of the industrial revolution, which marks the time when human alterations of the carbon cycle began in earnest. Adopting this pre-industrial case as our steady state has another advantage in that we know the history of CO₂ emissions from human activities pretty well and we know the present state of the carbon cycle pretty well and we even know the rate of change of various parts of the carbon cycle. Knowing these things about the carbon cycle, we can perform a useful test on our model of the carbon cycle. If we add to our steady state model the CO₂ emission history for the last 100 years, we should end up with a carbon cycle in its present state. This will provide us with a very nice way of assessing the significance of our modeling results.

To begin, we will make a survey of the various processes involved in the carbon cycle, dividing these processes into those that occur on land (the terrestrial realm), those that occur primarily in the oceans, and those related to human activities.

Processes of Carbon Flow in the Terrestrial Realm

Photosynthesis

Since its invention over 3 billion years ago, photosynthesis has been one of the most important processes on Earth, helping to make our planet different from all the other planets. The basic idea is that plants capture light energy and use it to split water molecules and then combine the products with carbon dioxide to make carbohydrates, which are used for fuel and construction of the plant; oxygen is a by-product of this reaction, which is summarized as:



This process takes place in the chloroplasts located in the interiors of leaves. Here, chlorophyll absorbs solar energy in the red and blue parts of the spectrum. This energy is

then used to split a water molecule into hydrogen and oxygen; in the process, the plants gain chemical energy that is used in a companion process that converts carbon dioxide into carbohydrates represented by CH_2O in the above equation.

The CO_2 used in this process gets into the interior of the leaf through small openings about 10 microns in diameter called stomata, which the plant can control like a valve, opening and closing to adjust the rate of transfer. The rate of CO_2 transfer is also a product of how much CO_2 is inside the leaf. For instance, if the interior of a leaf was filled with lots of CO_2 , then even if the stomata were wide open, little new CO_2 could enter the leaf -- it would be limited by how quickly the plant was consuming CO_2 in photosynthesis. Plants that are actively photosynthesizing generally have their stomata wide open, but there is sometimes a problem with this because with the stomata open, water from inside the plant escapes out into the air. As a consequence, when water is scarce, plants tend to close their stomata and thus they cannot photosynthesize at the maximum rate. Photosynthesis is also limited by the availability of other nutrients, especially nitrogen, which tends to be a limiting nutrient in many terrestrial ecosystems. However, as a general rule, if plants do have sufficient water, they will increase their rate of photosynthesis if there is more CO_2 in the air surrounding them — an effect known as ***CO₂-fertilization***. An interesting thing happens when the rate of photosynthesis increases; the leaf interiors are filled with more CO_2 , so the stomata close down to limit the intake of more CO_2 , and in doing this, the plant also limits the amount of water that can escape. What this amounts to is an increased efficiency of water use by the plants -- they grow more while using less water. But, there is an upper limit to this effect; at high levels of CO_2 , plants do not respond to additional increases in atmospheric CO_2 . Likewise, there is a lower limit to photosynthesis imposed by CO_2 levels, but we are not likely to approach such low levels in the next billion years or so (we will eventually have this problem since atmospheric CO_2 is slowly being drawn down through the precipitation of limestone).

Temperature is another important consideration in many life processes, and photosynthesis is no exception. As a general rule, the rates of most metabolic processes increase with temperature, but there is usually an upper limit where the high temperatures begin to destroy important enzymes, or otherwise inhibit life functions. For the majority of plants, this upper limit is not likely to come into play given the kinds of temperature changes we might expect in the space of a couple hundred years, so we can safely ignore it here (if our model does lead to temperature changes of greater than 10-20°C in a hundred years, we would presume that there is some problem with the model as this is unrealistic behavior). Another important reason to take temperature into account in our photosynthesis flow is that it turns out that in most environments, an increase in temperature correlates with an increase in precipitation, and since many regions where plants grow are somewhat limited by water, especially towards the end of the growing season, increased precipitation leads to a greater yearly rate of photosynthetic uptake of atmospheric carbon.

How will we keep track of the changing temperature? Recall that an increase in atmospheric CO_2 leads to an increase in the greenhouse effect and thus a warmer planet. One option is that we could attach our model of the carbon cycle to one of our models for the climate system. Another, simpler option is to develop a simple relationship based on

the known history of atmospheric CO₂ and global temperature. This has been done by a variety of people, and the result is an equation that looks like this:

$$\Delta T = 2.5 \times \frac{\ln\left(\frac{pCO_2}{290}\right)}{\ln(2)} \text{ } ^\circ\text{C}$$

Where ΔT is the temperature difference, in $^\circ\text{C}$, between the start and any time during the model simulation; \ln is the natural log; pCO_2 is the concentration of CO₂ in the atmosphere in ppm (parts per million); 290 is the concentration (ppm) of CO₂ in the atmosphere around 1890, when our model is set to begin. In this way, we monitor the temperature relative to the starting temperature (which we'll call 14 $^\circ\text{C}$). This logarithmic relationship means that for each doubling of CO₂, there is a 2.5 $^\circ\text{C}$ temperature increase.

Next, we must consider the problem of how to describe photosynthesis, globally, in the form of an equation that we can use in a model. We do get some help here from studies on a variety of different plants grown in greenhouses with varying levels of CO₂ and varying temperatures. We should realize, of course, that there are always uncertainties that arise when transferring results from the laboratory to the real world, and there are even more problems when you try to extrapolate to the scale of the whole world. The truth of the matter is that we don't know enough about the operation of our whole planet to solve this problem with confidence — the study of the global carbon cycle is in its early stages. And yet if we don't make some attempt to describe this process in the form of a global model, our understanding of the dynamics of the global carbon cycle will languish in the early stages. So we forge ahead.

The accumulated results indicate that our function for photosynthesis should satisfy the following characteristics:

- 1) the present day global flow should be 120 Gt C/yr (one gigaton of carbon per year; 1Gt = 10¹⁵g, also known as a *petagram*, Pg)
- 2) the rate should increase at higher atmospheric CO₂ levels, but there should be a saturation point, where additional increases in atmospheric CO₂ yield no further increase in the rate of photosynthesis
- 3) the rate should increase with increasing temperature.

There are several ways to construct an equation that incorporates this information, but here, we use the following equations, adapted from Gifford (1993):

$$F_p = \left(\frac{P_{\max} \times pCO_{2\text{eff}}}{K_{hs} + pCO_{2\text{eff}}} \right) \times \left(1 + (T_{sens_p} \times \Delta T) \right)$$

$$P_{\max} = \frac{\left(K_{hs} + (pCO_{2\text{init}} - pCO_{2\text{min}}) \right) \times F_{p\text{init}}}{\left(pCO_{2\text{init}} - pCO_{2\text{min}} \right)}$$

F_p is the global rate of photosynthetic uptake of CO₂ in GtC/yr.

P_{max} is a parameter with units of GtC/yr that is used to force the equation for F_p to give the proper value corresponding to the starting conditions of the model.

$K_{hs} = 72.5$ ppm — the half-saturation value — the atmospheric CO_2 concentration at which the rate of photosynthesis, F_p , is half of the ultimate saturation value, given that particular temperature

$pCO2_{init} = 290$ ppm — the pre-industrial (1880) atmospheric CO_2 concentration

$pCO2_{min} = 30$ ppm — value below which no photosynthesis can occur

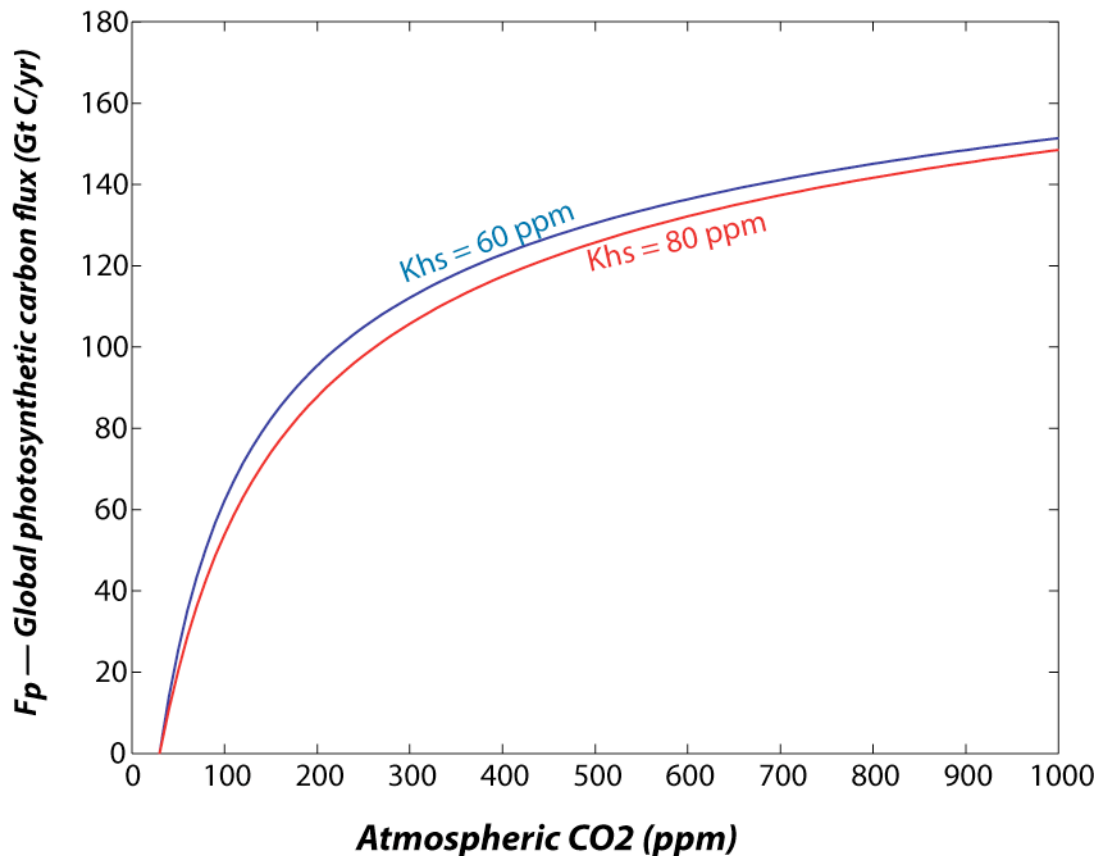
$pCO2_{eff} = pCO2 - pCO2_{min}$ — the effective atmospheric CO_2 concentration

$F_{p,init} = 100$ GtC/yr — the initial (pre-industrial) value for global photosynthesis

$Tsens_p = 0.04$ — establishes the increase of F_p per degree of warming

$\Delta T = T - T_{init}$ — temperature difference relative to initial temperature. T_{init} is set to 0

The figure below shows what the equation for F_p looks like with varying levels of atmospheric CO_2 (and thus varying temperatures too); this kind of curve is called a rectangular hyperbola and is typical of many biological processes that have a saturation effect.



We could just as easily devise a way of using graphical converters in STELLA to do the same job, but this equation will produce a smoother function and provides us with greater flexibility in modifying it during experiments. The K_{hs} parameter, the so-called half-

saturation value, is the atmospheric CO₂ concentration that corresponds to a rate of photosynthesis (F_p) that is half the ultimate saturation value. K_{hs} is a key parameter in defining the shape of the curve, which is always constrained to give a photosynthesis rate of 100 Gt C/yr when the atmospheric CO₂ concentration is 290 ppm — the starting (~1890) value.

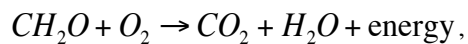
The temperature sensitivity part of the equation is simply a linear function, meaning that if you plot the temperature sensitivity versus the temperature, you get a straight line. The formulation here gives an increase in photosynthesis by a factor of 1.4 if the temperature increases 10°C. This is sometimes called the Q₁₀ for the process, and a Q₁₀ of 1.4 is in line with a variety of observations from experiments in greenhouses. It is important to note once again that there is an upper limit to this temperature sensitivity function in the real world, but we do not expect to approach it in this modeling exercise, so we will not try to incorporate it into our equation.

Defined in the manner outlined above, our photosynthesis flow is the same as what is commonly called Gross Primary Production. Gross Primary Production (GPP) differs from Net Primary Production (NPP), which is the gross minus respiration.

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Plant Respiration

If we think of photosynthesis as the process of making fuel, then respiration can be thought of as the process of burning that fuel — using it for maintenance and growth. This process can be described in the form of a reaction, just like photosynthesis. That reaction is:



which is effectively the reverse of photosynthesis. Through respiration, plants (and animals) release water and carbon dioxide. They also release energy, in the form of heat, or infrared radiation. Thus, the processes of living organisms represent a kind of energy flow system; energy flows in and energy of another form flows out. Do the carbon flows involved in respiration and photosynthesis balance each other as the equations seem to imply? The answer is no — otherwise, how could organisms grow?

Experiments on a variety of plants indicate that the ratio of photosynthesis to respiration is generally about 2 to 1, and this ratio does not appear to depend on the temperature. Or more precisely, the respiration does depend upon temperature, but in approximately the same way that photosynthesis does, so the ratio between them stays the same. When plants are young, and growing rapidly, but with not much biomass to maintain, this ratio is even higher; in older, larger plants, this ratio is lower since more carbon needs to go towards maintenance. For our purposes, we will assume that the global collection of plants has a ratio of about 2 to 1, so we will formulate plant respiration in the following manner:

$$F_{pr} = F_p * (50/100)$$

where F_{pr} is the rate of global plant respiration in Gt C/yr and F_p is the rate of global photosynthesis by land plants.

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Litter Fall (and below-ground addition to the soil)

Dead plant material enters the soil in two ways -- it falls on the surface as litter, and it is contributed below the surface from roots. The relative importance of these two pathways into the soil carbon reservoir vary according to the plants in an ecosystem, but it appears that the two are commonly about equal, which may seem a bit surprising since loss of organic carbon from root systems is a process that we generally don't see. In our model, we will lump these processes together and call them litter fall, keeping in mind that this is only half of the real story (later, we can enhance our model by breaking the soil up into several different boxes, and these two flows will no longer be lumped together). Litter fall is set to be the difference between the photosynthetic uptake of carbon and the return of carbon through plant respiration. If this were not the case, then the size of the land biota reservoir would be growing or declining, which may in fact be the case (it's doing both in different parts of the Earth), but we would like our model to be more or less in a steady state to begin with. In reality, it is the litter fall that is actually measured in studies of carbon flow through ecosystems. Litter fall combined with a measure of the gross primary productivity (the total amount of carbon used in photosynthesis) gives an estimate of the plant respiration flow according to the following equation:

$$\text{Gross Primary Productivity} = \text{Plant Respiration} + \text{Litter Fall}$$

Having already chosen the initial rates for photosynthesis and plant respiration, at 100 and 50, this leaves us with a value of 60 Gt C/yr for the rate of carbon added to the soil reservoir through the process of litter fall. But, we don't want this to be a constant value; it will undoubtedly change as a function of the size of the land biota reservoir. So, we can define this flow in the form of a standard draining flow:

$$F_{lf} = \text{land_biota} * (50/\text{INIT}(\text{land_biota}))$$

where F_{lf} is the flow in Gt C/yr and land_biota is the amount of carbon stored in the land biota (plants) at any given time.

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Soil Respiration

Respiration (sometimes called decay) also occurs within the soil, as microorganisms consume the dead plant material. In terms of a chemical formula, this process is the same as described above for plant respiration, only in this case, the microbes do not make the fuel themselves.

There is an unseen but fascinating universe of microbes living within the soil and they are the key means by which nutrients such as carbon and nitrogen are cycled through the soil system. A great diversity of microorganisms live in the soil — perhaps as many as 1000 species in a cubic centimeter — and they are capable of consuming tremendous quantities

of organic material. Much of the organic material added to the litter (the accumulated material at the surface of the soil) or within the root zone each year is almost completely consumed by microbes; thus there is a reservoir of carbon with a very fast turnover time — on the order of 1 to 3 years in many cases. The by-products of this microbial consumption are CO₂, H₂O, and a variety of other compounds, collectively known as humus. Humus is a much less palatable compound, as far as microbes are concerned, and is not decomposed very quickly. After it is produced at shallow levels within the soil, it generally moves downward and accumulates in regions of the soil with high clay content. Part of the reason it accumulates in the lower parts of the soil is that there tends to be less oxygen in that environment, and the lack of oxygen makes it even more difficult for microbes to work on this humus and decompose it further. But eventually, due to various processes that stir the soil, this humus moves back up to where there is more oxygen and then the microbes will eventually destroy the humus and release some more CO₂. This humus then constitutes another, longer-lived reservoir of carbon in the soil. ¹⁴C dates on some of this soil humus give ages of several hundred to a thousand years old. Taken together, the fast and slow decomposition processes, both driven by microbes, lead to an average residence time of around 20 to 30 years for most soils. The data used in our global carbon cycle model lead to a residence time of about 26 years for the global soil carbon reservoir.

These microbes (considered in terms of their respiratory output) are very sensitive to the organic carbon content of the soil as well as the temperature and water content, respiring faster at higher carbon concentrations, higher temperatures and in moister conditions (although if the soil is flooded with water, conditions are worse since no oxygen can get into the soil -- the majority of the microbes need oxygen to respire, as can be seen from the general equation for respiration given under the discussion of plant respiration). Studies seem to indicate that the soil respiration is in fact even more sensitive to temperature than photosynthesis and plant respiration. In general, higher temperatures tend to correspond with higher rates of precipitation, so we can consider the affects of water to go hand in hand with temperature. In our model of the carbon cycle, we will use an expression for soil respiration that takes these observations into account:

$$F_{sr} = Soil \times \left(\frac{49.4}{INIT(Soil)} \right) \times (1 + (Tsens_{sr} \times \Delta T))$$

$$Tsens_{sr} = 0.10 \text{ to } 0.01$$

The temperature sensitivity part of the equation is a linear function like that used in defining photosynthesis. The Tsens_{sr} value of 0.1 gives an increase in soil respiration by a factor of 2.0 if the temperature increases 10°C. This gives a Q₁₀ of 2.0 and is in line with a variety of observations (which generally are not in close agreement; this is not a well-constrained part of the model). In our initial model, we'll set this to 0.03, because it gives a better match with the observed record of atmospheric CO₂. It is important to note once again that there is an upper limit to this temperature sensitivity function in the real world, but we do not expect to approach it in this modeling exercise, so we will not try to incorporate it into our equation.

Permafrost — an Unknown

In recent years, increasing attention has been directed at permafrost soil carbon since the polar regions are warming much faster than the rest of the globe. As the permafrost melts, carbon that was added to these soils by processes like litter fall, will become available for soil microbes to respire and release to the atmosphere. In fact, it is almost surely happening already, but given that much of the permafrost is still frozen, we have probably not seen the real manifestation of this source of carbon. Estimates are variable, but a figure like 1000 to 1500 Gt of carbon reflects the current thinking; this is a huge amount of carbon and has the potential to significantly alter the future of atmospheric CO₂ levels. As the permafrost begins to melt, some estimates are that it will contribute something in the range of 2-5 Gt C/yr, which is large compared to the human-related changes. Of course, some of this released carbon will be offset by new carbon sequestered into these formerly frozen soils, but initially, the system will not be in equilibrium and these regions can be expected to be a net source of CO₂ to our atmosphere.

This process could be added to the model by first creating a new reservoir called *PERMAFROST C* and then adding a flow from it to *ATMOSPHERE*. The flow, which might be called melting could be defined as follows:

$$F_{pf} = .05 * \left(\frac{PermafrostC}{INIT(PermafrostC)} \right) * (1 + (Tsens_{pf} \times \Delta T))$$

$$Tsens_{pf} = 40$$

Here, the initial flow value is set to be very small, such that at the start of the model, this is an insignificant flow. The temperature sensitivity here is very large, but this creates a flow of around 3-4 Gt C/yr with the kinds of warming we expect by the end of the century.

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Runoff

Although most of the carbon loss from the soil reservoir occurs through respiration, some carbon is transported away by water running off over the soil surface. This runoff is eventually transported to the oceans by rivers. The actual magnitude of this flow is a bit uncertain, although it does appear to be quite small. The most recent estimates place it at 0.6 Gt C/yr; we'll defined this as a standard draining process (first-order kinetic process) as follows:

$$F_r = Soil \times \left(\frac{0.6}{INIT(Soil)} \right)$$

where F_r is the runoff flow to the ocean in GtC/yr.

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Processes of Carbon Flow in the Oceanic Realm

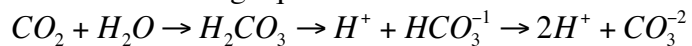
Ocean - Atmosphere Exchange

Carbon dioxide can be dissolved in seawater, just as it can be dissolved in a can of soda; it can also be released from seawater as the CO₂ from a soda can also be released. This transfer of gas back and forth between a liquid and the atmosphere is an extremely important process in the global carbon cycle since the oceans are such an enormous reservoir with the potential to store and release significant quantities of CO₂. In general, this flow depends on the concentration of CO₂ in the atmosphere and the oceans, but it gets a little complicated because the concentration of CO₂ in seawater depends on a number of other factors. To understand this process, we need to have some sense of what happens to CO₂ once it gets dissolved in seawater.

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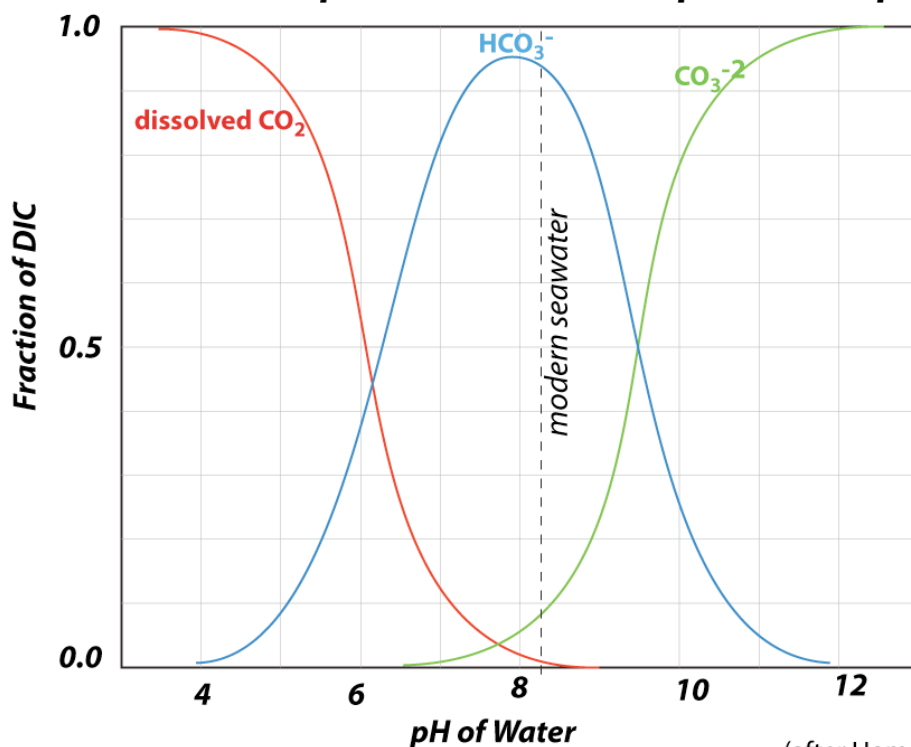
Carbonate Chemistry of Seawater

When CO₂ enters seawater, it reacts with water and forms a series of products, as described in the following equation:



This means that in seawater, you can find all of these different forms or species of carbon co-existing, but in reality, bicarbonate (HCO₃⁻) is the dominant form of inorganic carbon; carbonate (CO₃²⁻) and dissolved CO₂ are important, but secondary (see Figure 7.04).

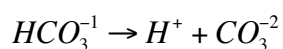
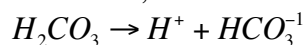
Relationship between Carbon Species and pH



(after Homen, 1992)

Figure 7.04 The relative proportions of the different carbon species depends on the alkalinity and the total DIC; these proportions in turn determine the pH. Salinity and temperature also exert some control on the proportions of carbon species. In the oceans today, most of the carbon is in the form of HCO_3^- , with relatively small amounts of CO_3^{2-} and dissolved CO_2 .

In the above equation, the double-headed arrows mean that the reactions can go in both directions and generally do until some balance of the different compounds is achieved -- a chemical equilibrium. Each of these reactions has associated with it an equilibrium constant, which establishes the relative concentrations of the compounds on either side of the reaction. For instance, if we isolate two of the above reactions,



we can say that the equilibrium constants, k_1 and k_2 , are given by a ratio formed by the concentrations of the various compounds involved:

$$k_1 = \frac{[\text{H}][\text{HCO}_3]}{[\text{H}_2\text{CO}_3]}, \quad k_2 = \frac{[\text{H}][\text{CO}_3]}{[\text{HCO}_3]} \quad (1)$$

We can do some algebra with these equations, just like normal equations. Our goal is to find an expression for the concentration of H_2CO_3 , so we begin by rearranging the equation on the left above (1) to the following form:

$$[H_2CO_3] = \frac{[H][HCO_3^-]}{k_1} \quad (2)$$

Then we rearrange the right side of (1) so that it becomes:

$$[H] = \frac{k_2[HCO_3^-]}{[CO_3^{2-}]} \quad (3)$$

If we know or calculate the concentration (or activity) of hydrogen — [H] — it is an easy step to get the pH of the seawater, just take the negative log of [H], which our model can keep track of. Next, we substitute (3) into (2), to give us our desired equation expressing H_2CO_3 in terms of HCO_3^- and CO_3^{2-} .

$$[H_2CO_3] = \frac{k_2}{k_1} \left(\frac{[HCO_3^-]^2}{[CO_3^{2-}]} \right) \quad (4)$$

Ultimately, we want to get an expression for the concentration of CO_2 gas contained in the seawater at equilibrium; this is usually expressed as the partial pressure of CO_2 , with units of μatm (micro-atmospheres), or ppm (parts per million, by volume) rather than a typical concentration, which would have units of moles per cubic meter of water. The partial pressure is given by the following formula:

$$pCO_2 = K_3[H_2CO_3] \quad (5)$$

in which K_3 is a slightly different kind of equilibrium constant that incorporates the solubility of CO_2 in seawater, which is a function of temperature and salinity. Our next step is to combine the various equilibrium constants into a single value as:

$$KCO_2 = K_3 \times \frac{k_2}{k_1} \quad (6),$$

keeping in mind that this value will be a function of temperature (also salinity). Then we can substitute (4) and (6) into (5) to obtain another expression for the partial pressure of carbon dioxide gas in seawater:

$$pCO_2 = KCO_2 \times \left(\frac{[HCO_3^-]^2}{[CO_3^{2-}]} \right) \quad (7)$$

The next thing we need to do is to find expressions for the concentrations of carbonate and bicarbonate in terms of the total amount of carbon dissolved in seawater, which will change over time as the oceans release or absorb CO_2 from the atmosphere. First, we need to define a term for the total concentration of inorganic carbon in solution:

$$\Sigma CO_2 = [HCO_3^-] + [CO_3^{2-}] \quad (8)$$

This is an approximation since it ignores CO_2 gas and H_2CO_3 , but both of these are very minor components. This sum, the concentration of total dissolved carbon, is simply equal to the amount of carbon in the ocean reservoir divided by the volume of the ocean. Looking at the above equation, we see that it does not tell us the relative proportions of

the carbonate and bicarbonate — just their combined concentration. So, we need to find some other means of establishing the proportions of these two forms of carbon. We get some help from the fact that the relative proportions of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) play an important role in establishing the balance of positive and negative charges in seawater. Ions like calcium (Ca^{2+}), sodium (Na^+), , potassium (K^+), and magnesium (Mg^{2+}) all add positive charges to seawater; these are partially countered by chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), and bromide (Br^-) ions, but the result is a slight deficit of negatively charged ions. This difference is essentially made up by the carbonate and bicarbonate ions. If more negative charge is needed, then more of the carbon occurs in the form of carbonate since it has a charge of minus 2, while if less negative charge is needed, more of the carbon exists in the form of bicarbonate. The excess positive charge of seawater that needs to be balanced by the different forms of dissolved carbon is called the alkalinity of the seawater. The alkalinity is defined as:

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (9)$$

Note that the carbonate ion counts twice since it has a minus 2 charge. It is important to realize that the total alkalinity is really determined by the other ions in solution — the ones mentioned above. This means that for the purposes of our model, we can keep the alkalinity constant, although we could define slightly different alkalinities for the warm and cold surface waters of the oceans if we made a more elaborate model. Looking at the above equation, you can see that with a given alkalinity, if we have just a little dissolved carbon, more of the carbon will be in the form of the carbonate ion (CO_3^{2-}) in order to make up the charge imbalance, but if we have a high concentration of dissolved carbon, there will be a greater proportion of the bicarbonate ion (HCO_3^-). The concentrations of both the carbonate and bicarbonate ions can be expressed as a function of both the alkalinity and the concentration of total dissolved inorganic carbon, ΣCO_2 , as shown in the following:

$$\begin{aligned} [\text{CO}_3^{2-}] &= \text{Alk} - \Sigma\text{CO}_2 \\ [\text{HCO}_3^-] &= 2\Sigma\text{CO}_2 - \text{Alk} \end{aligned} \quad (10)$$

Here, we need to remember that this is an approximation because we ignored the term for H_2CO_3 in equation (8). In the model we will eventually experiment with, we use a more precise formulation that does not ignore the concentration of H_2CO_3 . This increases the complexity of the algebra, giving us a quadratic equation whose solution ends up as:

$$\begin{aligned} [\text{HCO}_3^-] &= \frac{\Sigma\text{CO}_2 - \sqrt{\Sigma\text{CO}_2^2 - \text{Alk}(2\Sigma\text{CO}_2 - \text{Alk})} \times \left(1 - 4 \frac{k_2}{k_1}\right)}{\left(1 - 4 \frac{k_2}{k_1}\right)} \\ [\text{CO}_3^{2-}] &= \left(\frac{\text{Alk} - [\text{HCO}_3^-]}{2}\right) \end{aligned} \quad (11)$$

Regardless of whether we consider the more digestible form (10) or the more precise form of expressing HCO_3^- and CO_3^{2-} (11), we are finally set, because if we look at the equation for the partial pressure of CO_2 ,

$$p\text{CO}_2 = K\text{CO}_2 \times \left(\frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]} \right) \quad (7)$$

we see that all of the terms can be expressed in terms of components of the model. We have reached the light at the end of the algebraic tunnel.

As can be seen, the chemistry of carbon in seawater is relatively complex, but it turns out to be extremely important in governing the way the global carbon cycle operates and explains why the oceans can swallow up so much atmospheric CO_2 without having its own CO_2 concentration rise very much.

Summary of Carbonate Chemistry

Let's see if we can summarize this carbonate chemistry — it is important to have a good grasp of this if we are to understand how the global carbon cycle works.

- Carbon can exist in three main inorganic forms in sea water — CO_2 , HCO_3^- , and CO_3^{2-} , and there is a rapidly-achieved equilibrium between these species.
- The ratio of HCO_3^- to CO_3^{2-} along with the water temperature determines the CO_2 concentration of seawater and also the pH.
- The alkalinity of sea water represents the positively-charged ions that need to be countered by negatively-charged carbonate ions.
- The concentration of the total dissolved inorganic carbon (DIC), along with the alkalinity determines the ratio of HCO_3^- to CO_3^{2-} , and thus the CO_2 concentration of seawater. If we increase DIC without changing the alkalinity, then more carbon must be in the form of HCO_3^- , which increases both pH and the CO_2 concentration of seawater.
- The CO_2 concentration of seawater, relative to the atmospheric CO_2 , determines whether the oceans absorb or release CO_2 . Currently the cold parts of the oceans absorb atmospheric CO_2 and the warm regions of the oceans add CO_2 to the atmosphere.
- The ability of carbon to switch back and forth between these three forms means that only a portion of the CO_2 absorbed by the oceans will remain as CO_2 .

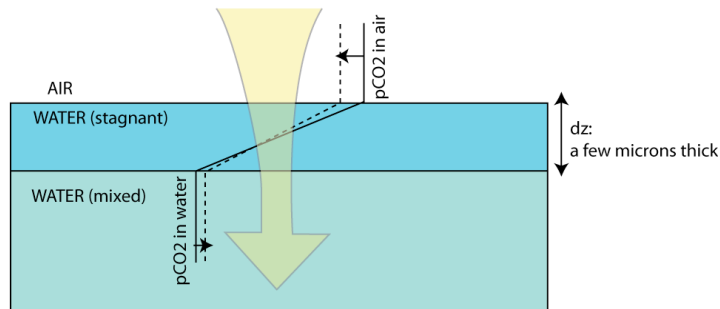
We now move on to find an expression for the actual rate of transfer of CO_2 back and forth across the interface between the air and the oceans.

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Ocean - Atmosphere Exchange Revisited

The exchange of gas between the air and the sea is, in theory, governed by the rate of diffusion and the distance the diffusion has to cover, as indicated the figure below.

Air - Sea Carbon Dioxide Exchange



Here, the atmosphere has a higher concentration of CO₂ than the ocean, so it will flow into the ocean at a rate governed by the diffusion constant and the concentration gradient:

$$\frac{dC}{dt} = D \times \left(\frac{C_{atm} - C_{oc}}{dz} \right)$$

If the concentration gradient goes the other way — higher in the water than the air — the flow of CO₂ goes up into the air.

As depicted in the figure above, the concentrations in the air and the sea are relatively constant (spatially, not temporally) since these two media undergo rapid and turbulent mixing that would tend to even out any systematic variations. The exception to this is a thin layer of water, just 20 to 40 microns thick, which, because of the surface tension of the water, is unable to mix well. This stagnant film is the barrier across which the diffusion has to occur. The rate of gas transfer, or flux, is given by the equation shown in the figure. The units of the diffusion coefficient are in m²/yr and the units of the concentrations would be given in units like g/m³, so the overall units are in g/m²yr. When this quantity is multiplied by the area of the ocean, then we have the overall rate of transfer in g/yr. In our model, we will represent this process in the following way:

$$F_{ao} = k_{ao} (pCO2_{atm} - pCO2_{oc})$$

$$k_{ao} = 0.278 \text{ (Gt C yr}^{-1} \text{ ppm}^{-1}\text{)}$$

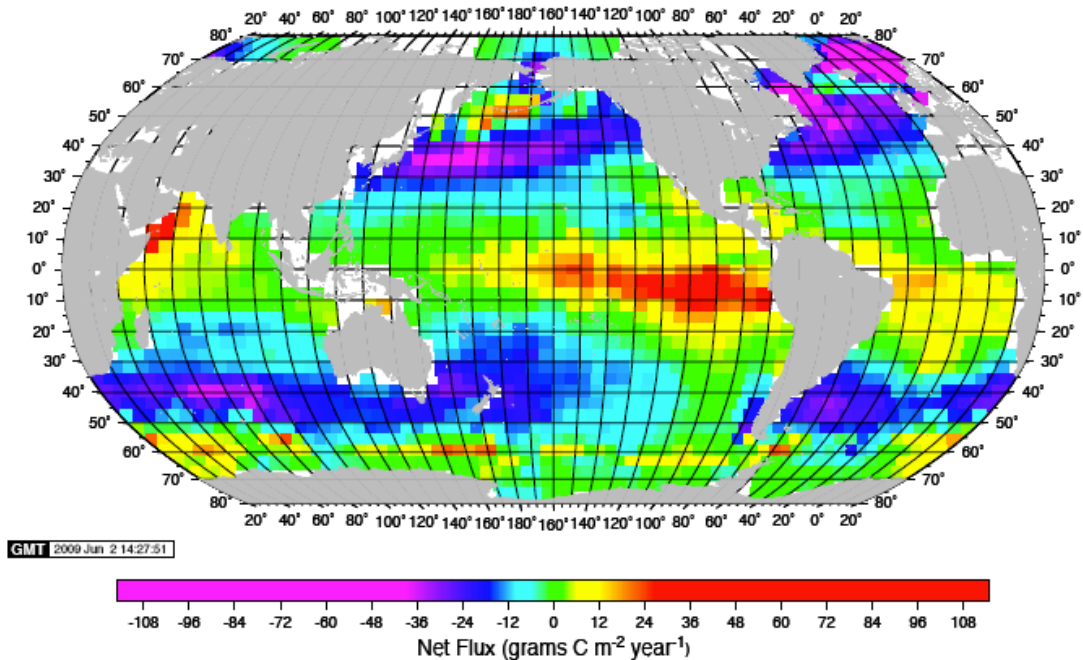
The constant we use here, k_{ao} , combines the diffusion constant, the stagnant film thickness and the area of the oceans. We will take this to be a constant value, but it is important to consider that it includes incorporates the stagnant film thickness, which is related to wind velocity. Higher velocity winds will lead to a thinner stagnant film and thus the gas transfer will be faster.

How has this coefficient been determined? Several methods have been used, but one of the more interesting involves the use of extra ¹⁴C that was generated by atmospheric nuclear explosion tests. These tests stopped in about 1963, and since that time, the abundance of ¹⁴C in the atmosphere has steadily declined. Part of the decline is due to radioactive decay, but a major part of the decline is due to absorption by the oceans. The abundance of ¹⁴C in seawater, and its distribution with depth are observations that provide

enough information to determine the coefficient of gas transfer. This effectively amounts to using the bomb-generated ^{14}C as a tracer in the sea — an unexpected benefit from the nuclear weapons program.

In the real world, there are important variations in the gas transfer between the ocean and atmosphere, which can be seen in the figure below, which represents a kind of snapshot of this transfer across the globe. The units here are grams of C per m^2 per year and each box is about $1\text{e}6 \text{ m}^2$. The red, orange, and yellow colors represent places where the oceans are giving up CO_2 to the atmosphere; the blue and purple areas are places where the oceans are sucking up atmospheric CO_2 . Summing these up, we find that the oceans are taking up around 92 Gt C/yr and they are releasing about 90 Gt C/yr — for a net flow of 2 Gt C/yr into the oceans. This exchange is variable in space and time, but a few general features can be pointed out. In general, the colder parts of the oceans absorb CO_2 and the warmer parts release CO_2 into the atmosphere. This makes sense because CO_2 is more soluble in colder water another way to say this is that the equilibrium constants in the carbonate chemistry reactions described above are sensitive to temperature such that at colder temperatures, more of the carbon is in the other carbon species, so the pCO_2 of the ocean water is lower when the temperature is colder. One exception is the ocean around Antarctica, where the water is cold and yet it releases a good deal of CO_2 to the atmosphere; the reason for this is that there is upwelling of deep water in that zone and the deep ocean has much higher pCO_2 values than the surface waters, largely due to the effects of the biological pump.

Mean Annual Air-Sea Flux for 2000 [Rev Jun 09] (NCEP II Wind, 3,040K, $\Gamma=26$)



http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/pages/air_sea_flux_2000.html

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Marine Biota Exchange — The Biologic Pump

The surface waters of the world's oceans are home to a great number of organisms that include photosynthesizing phytoplankton at the base of the food chain. These plants (and cyanobacteria) utilize CO₂ gas dissolved in seawater and turn it into organic matter, and just like land plants, these phytoplankton also respire, returning CO₂ to the surface waters.

At the same time, many planktonic organisms extract dissolved carbonate ions from seawater and turn them into CaCO₃ shells. When these planktonic organisms die, their soft parts are mainly consumed and decomposed very quickly, before they can settle out into the deeper waters of the oceans. This decomposition thus returns carbon, in the form of CO₂, to seawater. The net transfer, then is defined in our model as follows:

$$F_{ob} = 10 * \left(\frac{OceanBiota}{INIT(OceanBiota)} \right)$$

However, some of the organic remains and the inorganic calcium carbonate shells will sink down into the deep oceans, thus transferring carbon from the shallow surface waters into the huge reservoir of the deep oceans. This transfer is often referred to as the *biologic pump*, and it causes the concentration of CO₂ gas, and also DIC (ΣCO_2), the concentration of total dissolved inorganic carbon in the surface waters to be less than that of the deeper waters. This can be seen in Figure 7.08, which shows the vertical distribution of ΣCO_2 (and also alkalinity) in a profile view for some of the major regions of the world's oceans.

Profiles of Alkalinity and DIC (ΣCO_2) in the World's Oceans

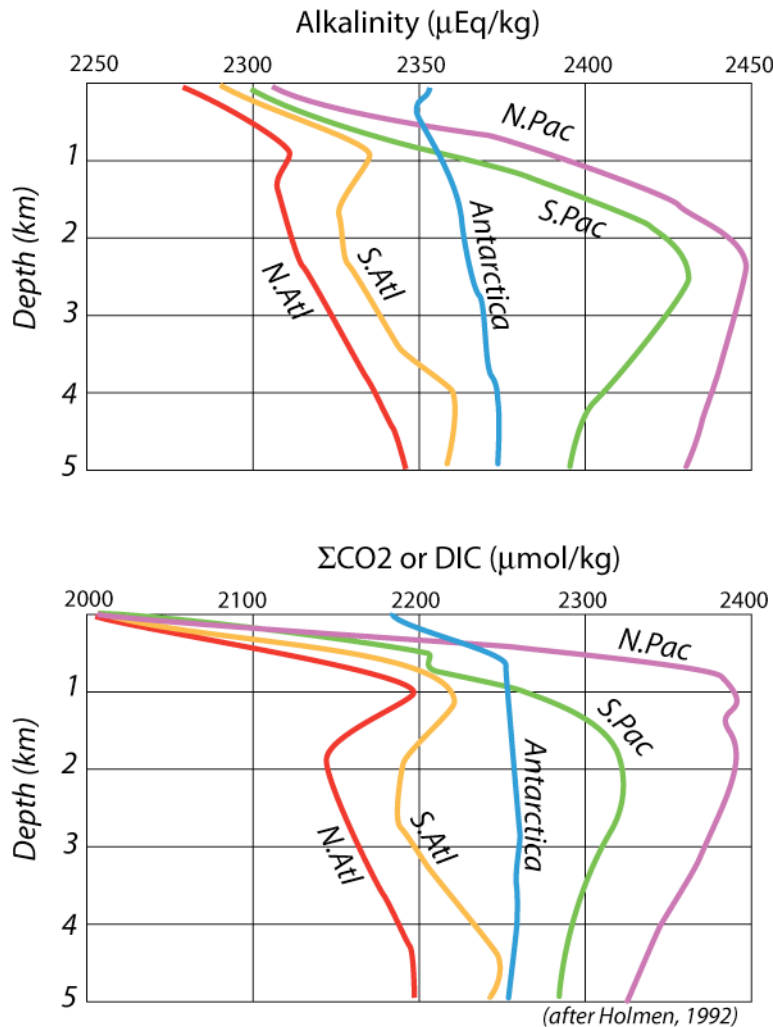


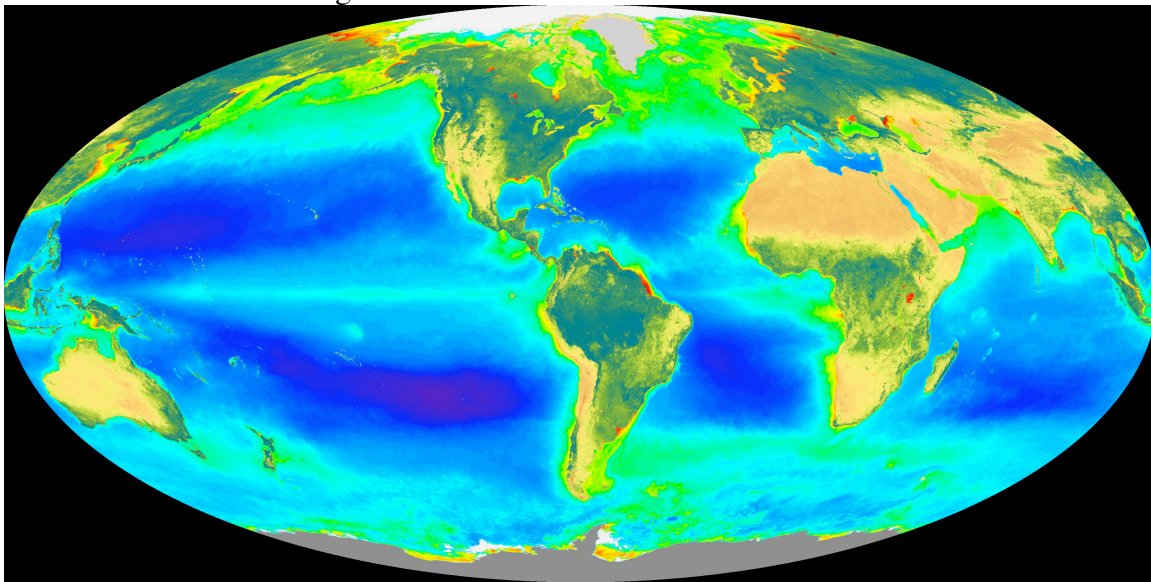
Figure 7.08 Representative vertical profiles of alkalinity and concentration of total inorganic carbon (DIC or ΣCO_2) from the world's oceans. In general, the surface waters are depleted in alkalinity and DIC because of the biologic pump, which exports carbon (both inorganic and organic) from the surface waters to the deep ocean. The carbonate portions of the marine biota dissolve in the deep waters and release Ca^{2+} ions, thereby increasing the alkalinity of the deep ocean, and at the same time, depleting the alkalinity of the surface ocean.

Why is the alkalinity reduced in the surface waters? For the same reason that DIC (ΣCO_2) is depleted. Planktonic organisms make shells of CaCO_3 , and when these sink to the seafloor, they carry Ca^{2+} ions with them, thus reducing the alkalinity. Much of this CaCO_3 is later dissolved when it reaches deeper parts of the oceans, which explains the higher alkalinity values in the deep waters, as seen in Figure 7.08. By controlling the concentration of CO_2 gas dissolved in the surface waters, the planktonic organisms exert a strong influence on the concentration of CO_2 in the atmosphere. For instance, if the biologic pump were turned off, atmospheric CO_2 would rise to about 500 ppm (relative to

the current 350 ppm); if the pump were operating at maximum strength (i.e., complete utilization of nutrients), atmospheric CO₂ would drop to a low of 140 ppm. Clearly, this biologic pump is an important process. In our model, the pump is defined as follows:

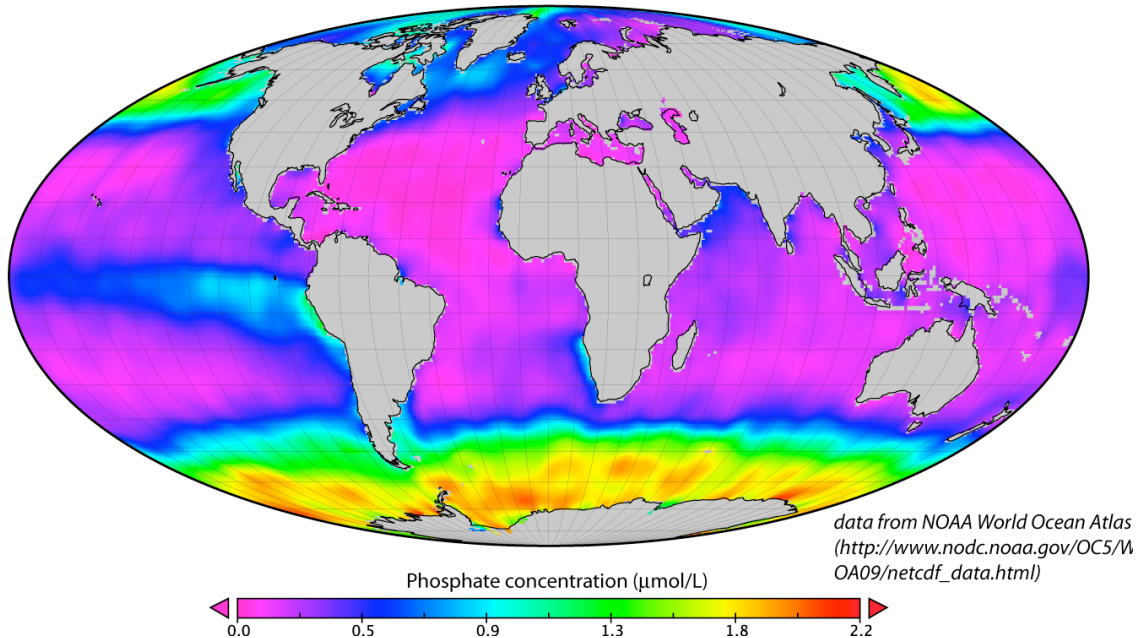
$$F_{bp} = 10 \times \left(\frac{OceanBiota}{INIT(OceanBiota)} \right)$$

What controls the strength of this biologic pump? The photosynthesizing plankton require nutrients in addition to CO₂ in order to thrive; specifically, they require nitrogen and phosphorus. Most of these plants need P, N, and C in a ratio of 1:16:125 and since at present, the ratio of P to N in ocean water is about 1:16, both P and N limit the growth of these phytoplankton. Photosynthetic activity of plankton can be mapped out by satellites tuned to record differences in water color due to the presence of chlorophyll. This distribution is shown in Figure 7.09 below.



If the nutrients in seawater were being utilized to the maximum extent possible, there would be practically no P and N dissolved in seawater, but in fact, as shown by the figure below, the concentration of P tells us that the biologic pump is not operating at maximum efficiency. In the map below, the purple regions represent regions with no phosphate in the surface water of the oceans, meaning that there is simply a lack of nutrients, or that all the nutrients are utilized. In particular, it is the cold, polar regions that are not utilizing all of the available nutrients. This may be due in part to the temperature, but it may also be related to a paucity of iron, a minor nutrient that is apparently lacking in the colder regions, especially in the southern ocean ringing Antarctica.

Ocean Phosphate Concentration



We might wonder whether or not it is likely that global warming might lead to a greater utilization of nutrients by the marine biota. If so, this would lead to a more vigorous biologic pump in the oceans that might tend to limit the increase of atmospheric CO_2 . It seems plausible given the observation that in today's ocean, there is greater nutrient utilization in areas where the ocean is warmer. Is there a record of this in the past?. Since it is now much warmer than it was during the last glaciation, we might investigate whether the biological pump was any weaker then relative to the present. Not surprisingly, people have looked into this question and the data indicate that the pump was, if anything, *slightly* stronger during the last glaciation. How is this known? It is based on record of the ratio of different isotopes of carbon, preserved in the shells of plankton that were deposited on the seafloor. Intense biological productivity in the surface waters alters -- relative to the rest of the ocean -- the carbon isotope ratio because organisms have a strong preference for one isotope of carbon (^{12}C) than another (^{13}C). The magnitude of this isotope shift is then a function of how intense the biological pump has been.

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Downwelling

As mentioned above, downwelling transfers cold surface waters into the deep interior of the oceans, and as a result, carbon is transferred as well. The magnitude of the flow is thus a function of the volume of water flowing and the average concentration of carbon in the cold surface waters, which is itself a function of the total amount of carbon stored in this reservoir, assuming that the size of the reservoir is not changing appreciably over the few hundred years that this model is intended to be used for.

Downwelling occurs primarily near the poles, where surface waters are strongly cooled by contact with the air. This cooling leads to a density increase. The formation of ice from seawater at the margins of Antarctica increases the salinity of the seawater there, adding to the density of the water. This dense water then sinks and flows through the

deep oceans, effectively mixing them on a timescale of about 1000 years or so (the Atlantic Ocean mixes somewhat faster, which helps explain the smaller ΣCO_2 and alkalinity gradients seen in Figure 7.08). In our model, the flow of carbon from the cold, shallow water to deep water will simply be a function of how much carbon is stored in the cold surface water reservoir. This implies that we are not altering the volumetric flow of downwelling water, which is probably acceptable if we are only concerned with a few hundred years. In the form of an equation, this flow is:

$$F_{\text{down}} = 90.6 * \left(\frac{\text{SurfOcean}}{\text{INIT}(\text{SurfOcean})} \right)$$

where F_{down} is the flow of carbon due to downwelling, in Gt C/yr. This equation is set so that at the beginning of the model, the magnitude of this flow will be 90.6, which is within the range of current estimates, adjusted here to make the system be in a steady state.

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Upwelling

Upwelling is the converse of downwelling, and as the deep waters rise to the surface, they bring with them carbon. The total transfer of carbon is thus a function of the volume of water involved in this flow and the amount of carbon stored in the deep ocean reservoir. Upwelling occurs in areas of the oceans where winds and surface currents diverge, moving the surface waters away from a region; in response, deep waters rise up to fill the "void". Upwelling occurs along the equator, where there is a strong divergence, and also along the margins of some continents, such as the west coast of South America. This upwelling water also brings with it nutrients such as nitrogen and phosphorus, making these waters highly productive.

We will define the flow of carbon resulting from upwelling in a like manner to the downwelling flow:

$$F_{\text{up}} = 100 * \left(\frac{\text{DeepOcean}}{\text{INIT}(\text{DeepOcean})} \right)$$

Note that the amount of carbon transferred by this flow is greater than the downwelling flow. This is not because the volume of flow is different in these two processes, but rather because the concentration of carbon in the deep waters of the ocean is greater than that in the shallow surface waters, due in part to the operation of the biologic pump mentioned above.

To make our model simpler, we combine the upwelling and downwelling flows into one flow called *ocean mixing*, which is defined as follows:

$$F_{\text{omx}} = F_{\text{up}} - F_{\text{down}}$$

The flow is defined as a biflow, meaning that depending on the sign of this difference, carbon can move either way.

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Sedimentation

Some of the carbon, both organic and inorganic (i.e., calcium carbonate shells) produced by marine biota and transferred to the deep oceans settles out onto the sea floor and accumulates there, eventually forming sedimentary rocks. The magnitude of this flow is small -- about 0.6 Gt C/yr -- relative to the total amount transferred by sinking from the surface waters -- 10 Gt C/yr. The reason for this difference is primarily because the deep waters of the oceans dissolve calcium carbonate shell materials; below about 4 km, the water is so corrosive that virtually no calcium carbonate material can accumulate on the sea floor. In addition, some of the organic carbon is consumed by organisms living in the deep waters and within the sedimentary material lining the sea floor. This consumption results in the release of CO₂ into the bottom waters and thus decreases the amount of carbon that is removed from the ocean through this process. It is worth noting that the process of organic carbon consumption on the seafloor is another microbial process and is very similar to the soil respiration flow described above. Since the microbes living on the seafloor require oxygen to accomplish this task, the supply of oxygen to the seafloor by deep currents is an important part of this process.

We will define the sedimentation flow to be a fixed percentage of the amount of carbon transferred to the deep waters by the biologic pump flows from the shallow marine biota reservoirs. The equation for this flow is thus:

$$F_{sed} = 0.6 \times \left(\frac{BioPump}{10} \right)$$

where F_{sed} is the transfer of carbon from the deep ocean reservoir to the sedimentary rock reservoir, and *BioPump* the flow of carbon from the surface ocean biota. This equation is set up so that initially, with *BioPump* set to total 10 Gt C/yr, the F_{sed} flow will have a value of 0.6 Gt C/yr.

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Volcanism and Metamorphism

When sedimentary rocks deposited on oceanic crust are subducted, they may melt or undergo metamorphism; in either case, the carbon stored in calcium carbonate -- limestone -- is liberated in the form of CO₂, which ultimately is released at the surface. The CO₂ may come out when a volcano erupts, or it may slowly diffuse out from the interior via hot springs, but in both cases, it represents a transfer of carbon from the reservoir of sedimentary rocks to the atmosphere. The magnitude of this flow is quite small, and is adjusted here to a value of 0.6 Gt C/yr in order to create a model in steady state. This flow is defined as a constant in the model, although in reality, it will vary according to the timing of large volcanic eruptions. An extremely large volcanic eruption may emit carbon at a rate of around 0.2 Gt C/yr for a year or two, creating a minor fluctuation.

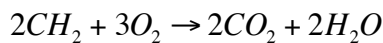
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Processes of Carbon Flow in the Human Realm

Fossil Fuel Burning

Another pathway for carbon to move from the sedimentary rock reservoir to the atmosphere is through the burning of fossil fuels by humans. Fossil fuels include petroleum, natural gas, and coal, all of which are produced by slow transformation of organic carbon deposited in sedimentary rocks -- essentially the fossilized remains of

marine and land plants. In general, this transformation takes many millions of years; most of the oil and gas we now extract from sedimentary rocks is on the order of 70-100 million years old. These fossil fuels are primarily composed of carbon and hydrogen. For instance, methane, the main component of natural gas, has a chemical formula of CH₄; petroleum can be represented by the formula of CH₂. The combustion of fossil fuels involves the use of oxygen and the release of carbon dioxide and water, as represented by the following description of burning petroleum:



Beginning with the onset of the industrial revolution at the end of the last century, humans have been burning increasing quantities of fossil fuels as our primary energy source. As a consequence, the amount of CO₂ emitted from this burning has undergone an exponential rise that follows the exponential rise in the human population. The magnitude of this flow is currently about 5 to 6 Gt C/yr. This number also includes the CO₂ generated in the production of cement, where limestone is burned, liberating CO₂.

This flow has changed considerably over time, as human population has increased and as our economies have become more industrialized with a big thirst for the energy provided from combustion of fossil fuels. Our model includes this history, beginning in 1880 and going up to 2010; beyond 2010 is the realm of future projections, which can be altered to explore the consequences of choices we might make or not make in the future.

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Land-Use Changes -- Forest Burning and Soil Disruption

The other form of human alteration of the global carbon cycle is through forest cutting and burning and the disruption of soils associated with agriculture. When deforestation occurs, most of the plant matter is either left to decompose on the ground or it is burned, the latter being the more common occurrence. This process reduces the size (the mass) of the land biota reservoir and the burning adds carbon to the atmosphere. Land-use changes other than deforestation can also add carbon to the atmosphere. Agriculture, for instance, involves tilling the soil, which leads to very rapid decomposition and oxidation of soil organic matter. This means that in terms of a system, we are talking about two separate flows here — one draining the land biota reservoir, the other draining the soil reservoir; both flows transfer carbon to the atmosphere. Current estimates place the total addition to the atmosphere from forest burning and soil disruption at around 1.5 Gt C/yr; estimates divide this into 70% to 50% forest burning, with soil disruption making up the remainder. The actual history of this alteration to the natural carbon cycle is not well-constrained — not nearly as well known as the fossil fuel burning history — but we include a reasonable history that reflects patterns of land settlement and forest clearing.

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