THE EARTH'S CARBON CYCLE

Chemical Engineering Course Material

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On three occasions in recent years, I have taught an elective course at the University of Notre Dame for chemical engineering seniors titled "Topics on Ecology and the Environment." I developed the course because I felt it was important for our students (and myself as well) to have a greater appreciation—from a chemical engineer's perspective—for the workings of Earth's natural processes, both biotic and abiotic, and a knowledge of how human and industrial activities are disturbing or might disturb them.

One of the significant components is a module on the carbon cycle—the subject of this article. In gathering and developing material for this module and others in the course, I was struck by these observations:

- *Many of the Earth's processes, including the carbon cycle, though fundamentally very complex in detail, can be represented by simple models that are useful for study purposes and even for quantitative estimates, at least as a first approximation.*
- *The development, analysis, and application of models are well within the scope of an undergraduate chemical engineering curriculum.*
- *The subject matter, or bits and pieces of it, can be integrated advantageously, straightforwardly, and nearly seamlessly into core chemical engineering courses.*

My objectives in this article are to demonstrate all of this, using the carbon cycle as the means, and to provide convenient material for others who may be persuaded by my third observation.

Of the biogeochemical cycles of the six major "life" elements, C, N, P, S, O, and H, the carbon cycle receives the lion's share of the attention in the literature. That's no surprise inasmuch as most of our energy needs are met by the burning of carbon-based fuels and inasmuch as the consequent increasing level of atmospheric carbon dioxide and its potential effect on the Earth's climate is a frequent focus of attention in technical and nontechnical publications. What's more, chemical engineers will have opportunities to play a prominent role in any steps taken to moderate that level, whether those steps be toward alternate energy sources or toward sequestering or otherwise preventing emissions directly into the atmosphere.

THE CONCEPTUAL MODEL

Carbon is found in all of Earth's compartments or reservoirs—in the biota and in the atmosphere, hydrosphere, and lithosphere. Mathematical models describing the cycle account for the movement of carbon among and within those reservoirs and for anthropogenic disturbances, which are principally due to fossil fuel burning and deforestation (*i.e.*, mainly burning of removed trees) for land use changes.

Figure 1 presents a schematic diagram of a conceptual model of the carbon cycle consisting of six reservoirs, numbered one through six. (A seventh reservoir for fossil fuels enters dynamically into the model later only as a disturbance to the six-reservoir natural cycle.) Other reservoirs, including sediments, marine biota, and lakes, rivers, and streams, are omitted for reasons given later. In one way or another, all models are based on this starting picture, which is sometimes

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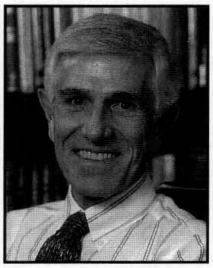

modified to include one or more of the omitted reservoirs. Models differ primarily in the extent of detail and correspondingly in the objectives of the modeler. For example, highly detailed climate studies employ general circulation models based on fundamental transport equations to describe processes in the atmosphere and/or ocean reservoirs and several types of vegetation to describe the atmosphere-biota exchange.[1] At the other extreme, so-called "box" (or "compartment" or "lumped") models that are intended to give estimates of global averages of carbon in major reservoirs, are based on spatially aggregated descriptions, often with no more detail, sometimes even less, than that shown in Figure 1.[2-7] Except to allude to the structure of high-end models and their purposes (and sometimes to compare results), I choose to work with simple box models in the course. In short, as tools for study, they have suited my purposes. Further, if properly calibrated and tuned, they have proven useful for quantitative purposes so long as the principal interest is in global averages, particularly in atmospheric carbon dioxide levels.

The conceptual model represented in Figure 1 and the mathematical description to follow are amalgamations of several box models that I have studied and used in the course. The version presented here is closely patterned after, but not identical to, that described in a recent publication by Lenton.[3] I usually have the students go through the development of other models as complementary outside work.

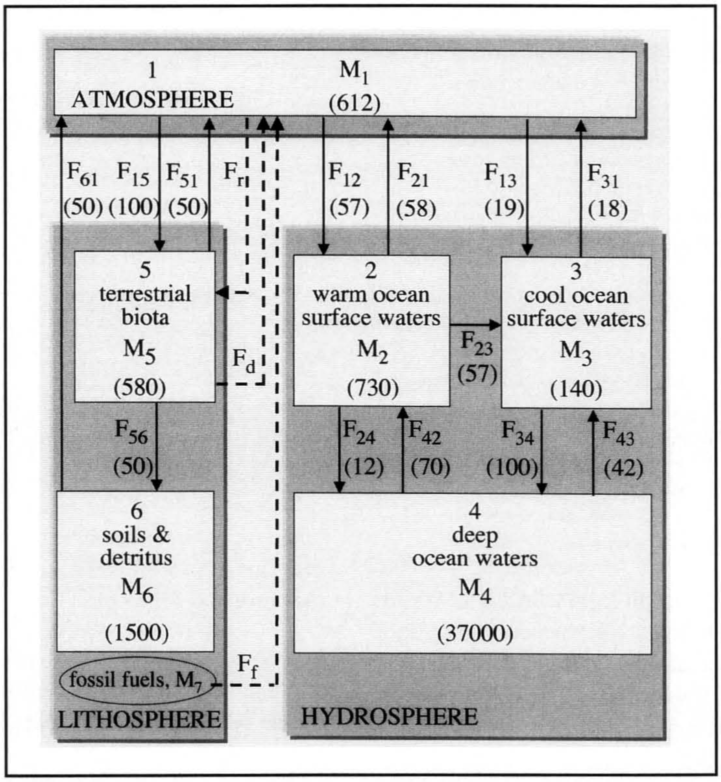

***Figure 1.** Schematic diagram of a six-box model of the carbon cycle. Values shown for reservoir masses (M_i, in PgC) and fluxes (F_{ij}, in PgC/y) are representative of the pre-industrial steady state (~1850).*

THE REFERENCE PRE-INDUSTRIAL STATE

The quantities shown in parentheses in the boxes in Figure 1 represent estimates of the "pre-industrial" distribution of carbon (*i.e.*, the mass of element C in all of its compounds) in petagrams (PgC, 1 Pg = 10^{15}g.) These are typical reference values presumed to represent the balanced (steady-state) conditions around the year 1850—early in the industrial revolution when there was little or no observable change from year to year.

The numbers in parentheses beside the arrows in Figure 1 represent estimates, in petagrams of carbon per year (PgC/y), of the transport (commonly termed "fluxes" in the relevant literature) of carbon between reservoirs. Such fluxes are estimates, adjusted so that each box is balanced at a steady state, where it would remain unless disturbed. There is no common agreement on the values of the reference pre-industrial masses and fluxes, or even on the reference year (generally between 1800 and 1860), but the variation from one reference source to another is of little significance. The values shown in Figure 1 are in line with those used in the references cited above.

M_1, the mass of carbon in the atmosphere reservoir can be taken to be entirely in the form of CO_2. The 612 PgC in that reservoir corresponds to a CO_2 concentration of 286 ppmv (parts per million by volume) —the concentration unit used in most illustrations to follow. (The conversion factor of 2.128 PgC/ppmv is based on a total atmosphere mass of 5.14 x 10^6 with a molecular weight of 29.)

Notice the notation in Figure 1. M_i stands for the mass of carbon in box i; F_{ij} for the flux of carbon from box i to box j. The anthropogenic disturbance flux F_f moves carbon from a nonrenewable fossil fuel reservoir to the atmosphere.* The other anthropogenic disturbances, F_d and F_r, take carbon from the renewable terrestrial biota reservoir to the atmosphere (deforestation) and from the atmosphere to the terrestrial biota (reforestation), respectively. (There is increasing interest in sequestering part of F_f by redirecting it to cavities in the lithosphere and/or to the deep ocean.[8,9] Those slight but interesting variations to the model will be mentioned in suggested exercises near the end.) The following list gives a succinct description of the other fluxes:

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* Actually, F_f accounts for all carbon emissions to the atmosphere except those due to deforestation. It is commonly termed "emissions due to fossil fuel burning"—a term that I shall use throughout. Other industrial sources, such as cement manufacturing, account for only a few percent of the total.

- F_{12}, F_{21}, F_{13}, and F_{31} are simply mass transfer rates for the exchange of carbon (as carbon dioxide in this case since nearly all atmospheric carbon is in that form) between the atmosphere and the ocean waters. Basically, the rates are described by the product of a mass transfer coefficient and a concentration driving force, but the nuances involved in using that description warrant further attention later.
- F_{23} represents the advective flow of carbon from the warm to cool surface ocean reservoirs. This flow, which accounts for most of the ocean mixing, results from the downflow of cool surface water at high latitudes and the corresponding upwelling to the warmer surfaces at low latitudes. There is also an eddy-mixing component contained in the fluxes between the surface and deep ocean waters. The model could be further simplified without affecting results noticeably by lumping boxes 2 and 3 into a single box.
- F_{15} is the rate of photosynthetic uptake of carbon from the atmosphere by terrestrial vegetation. This flux, assumed often in models of this type to be describable by a single overall rate expression, gets special attention later. M_5 is the total carbon in terrestrial biota, but we might think of it as being the mass of vegetation since about 90% of it is in forests.
- F_{56} is the flux of carbon in litter fall—mostly dead leaves and the like, but generally including all dead and waste products from the terrestrial biota.
- F_{51} and F_{61} are the fluxes of carbon, mostly as carbon dioxide with small amounts as methane and other compounds, to the atmosphere by biotic respiration.

As mentioned above, a more complete box structure would include additional elements for aquatic biota; sediments; and rivers, streams, and lakes. Such additions are more suited for discussions and assigned work than for incorporation into a working model for the following reasons: The inventory of carbon in aquatic biota and in rivers, streams, and lakes is negligibly small; sediments, the largest of all reservoirs with a total carbon mass of about 10^8 PgC, are the most sluggish by far; the small fluxes (~0.3 PgC/y) into and out of the sediments lead to a first-order time constant of the order of several hundred million years! For the reservoirs represented in Figure 1, first-order time constants, calculated as the ratio of the mass of carbon in a reservoir to the flux of carbon out of it, range from 1.19 years for the cool surface waters in box 3 to 330 years for the deep ocean waters in box 4. For the atmosphere, box 1, it's 3.48 years. The illustrations in simulations to come will cover time spans up to 250 years, over which time the sediment reservoirs are virtually steady.

THE EQUATIONS

The mathematical description of the box model of Figure 1 consists of a set of carbon balance equations. For the atmosphere, box 1, for example

$$\frac{dM_1}{dt} = F_{21} - F_{12} + F_{31} - F_{13} + F_{51} - F_{15} + F_{61} + \left(F_f + F_d - F_r\right) \qquad (1)$$

In general

$$\frac{dM_i}{dt} = \sum_{\substack{j=1 \\ j \neq i}}^{6} \left(F_{ji} - F_{ij}\right) + \textit{disturbances} \qquad (2)$$

If a particular F_{ij} does not appear in Figure 1, its value in Eq. (2) is zero. The disturbances, as represented in Figure 1, appear only in the balances for boxes 1 and 5.

To keep account of the fossil fuel supply, a seventh box is added, an out-of-cycle, nonrenewable reservoir of the carbon in fossil fuels. The following balance describes the depletion of that reservoir:

$$\frac{dM_7}{dt} = -F_f \qquad (3)$$

All terms in these equations have units of petagrams of carbon per year (PgC/y).

The initial conditions are the reference pre-industrial reservoir levels in 1850. I use 5300 PgC for the initial value of M_7, somewhat arbitrarily, but based on rather common statements that while the total carbon stored in fossil fuels is about 10,000 PgC, only about half of it can actually be recovered for use.

Since most of the reservoirs undergo relatively small changes over periods of interest, as later simulations will show, the fluxes can be related to the reservoir masses by first-order processes. That is

$$F_{ij} = k_{ij} M_i \qquad (4)$$

Such relationships are frequently employed in box models of the biogeochemical cycles, including the carbon cycle, with three exceptions: F_{15}, F_{21}, and F_{31}. For the others, the numerical value of k_{ij} can be obtained readily from the reference data given in Figure 1.

If the carbon in the ocean were present simply as carbon dioxide in aqueous solution, we would expect all four of the F's connecting the ocean surface waters to the atmosphere to be describable by Eq. (4)—under the safe assumption that Henry's law applies to the dilute CO_2 solution. The situation is complicated, however, by the fact that CO_2 in aqueous solution enters into equilibrium chemical reactions involving carbonate and bicarbonate forms. Therefore, while the fluxes F_{21} and F_{31} can be related linearly to aqueous CO_2, they are not linearly related to the total C; that is, to M_2 and M_3. The relationship to the total carbon in solution is complicated. It is affected by all of the factors that affect acid-base equilibrium in ocean water—total alkalinity, salinity, temperature, and dissolved salts of weak bases, such as boron. A rigorous treatment requires linking a set of equations for ocean chemistry dynamics to the above set. Some studies[3,5] have followed that procedure, as have I in some instances. Others[2,4,7] have opted for a simpler empirical approach that uses the following relationships:

$$F_{21} = k_{21} M_2^{\beta_2} \qquad F_{31} = k_{31} M_3^{\beta_3} \tag{5}$$

Values of the exponents β_2 and β_3, called buffer factors or Revelle factors, can be obtained from charts of the type given in the book by Butcher, *et al.*[10] They can also be obtained by delving into the intricacies of ocean chemistry dynamics and correlating results of calculations. I used the latter approach to obtain the values shown later, but to save space and to stay on track, I shall spare further detail.

My testing has shown that results of computations using constant values of the β's hardly differ from those obtained by appending detailed ocean dynamics to the model, so long as changes in M_2 and M_3 are relatively small, generally less than 5%. The numerical values of β range between 9 and 15; the nonlinearity is surprisingly strong. Notice that with values of β_2 and β_3 given, numerical values of the rate constants k_{21} and k_{31} can be determined from the reference conditions given in Figure 1.

The rate of photosynthetic uptake, F_{15}, of carbon from the atmosphere cannot be represented realistically as a linear function of M_1. The basic reason is that the function should account for a saturation effect with regard to the nutrient CO_2. That is, the rate increases with increasing CO_2 but approaches a limit. For small changes in M_1, the function may be approximated by a linear relationship, but as a later illustration will show, changes in M_1 are large over the periods of interest.

There seems to be no clear consensus as to what form to use for F_{15} in models of this type. Whatever the specific form, a common feature is a dependence on atmospheric carbon that suggests an ultimate saturation. The particular one chosen does not seem to be a critical matter so long as the constants are calibrated or tuned to fit existing data. Nevertheless, this is a fertile item for classroom discussion, debate, and outside work. Here I shall use the form employed by Lenton[3]

$$F_{15} = \begin{cases} k_{15} M_8 \dfrac{M - \gamma}{M_1 + \Gamma} & \text{for } M_1 > \gamma \\ 0 & \text{for } M_1 \le \gamma \end{cases} \tag{6}$$

where

- γ is the threshold value of M_1 (I used Lenton's value of 62 PgC.)
- Γ is a saturation parameter (Lenton used it as a tuning parameter and arrived at a value of 194 PgC. By methods described later, I arrived at a value of 198 PgC.)
- k_{15} is a rate coefficient to be calculated from the reference state.
- M_8 is a function that depends on the disturbances F_r and F_d as explained and described below. In short, it accounts for changes in the Earth's capacity for terrestrial biota.

The role of the function M_8 is important but not obvious at first glance, and definitions and explanations do not come easily. Let me first define it by way of the following equation and then offer brief explanations.

$$M_8(t) = 1 + \int_{1850}^{t} \frac{\left(k_r F_r - k_d F_d\right) dt}{M_{5,\text{ref}}} \tag{7}$$

where

- k_d is the fraction of forested area or mass (or forest capacity) that cannot be reforested (is not available for regrowth) following deforestation activities—for example, forest areas cleared for urban development.
- k_r is that fraction of the reforested area or mass that increases the Earth's capacity for terrestrial biota. (This is sometimes termed "aforestation" as opposed to "reforestation" that directly renews deforested areas.
- $M_{5,\text{ref}}$ is a normalizing factor inserted arbitrarily to make M_8 dimensionless. I take it to be the initial value of M_5.

Lenton used this form but did not include k_r and F_r explicitly in his formulation. Reforestation can be accounted for without those factors if F_d is allowed to have negative values. I prefer to show F_r and F_d separately for clarity in simulations later.

Simply stated, the integral in Eq. (7) accounts for permanent effects of the disturbances F_d and F_r. Were that integral not included, the model equations would lead to the following illogical conclusion, among others: If $F_f \equiv 0$, and if F_d and F_r eventually settle to zero, the ultimate steady state of carbon in the reservoirs would be identical to the starting reference state; the effects of the temporary nonzero values of the disturbances would die away, according to the model. But obviously the effects of some land use changes must persist—for example, if forest areas are cleared and urbanized with no offsetting reforestation. With the integral included in M_8 with $k_d \neq 0$ and $F_r \equiv 0$, such land use change would permanently affect the distribution of carbon, not its total amount. Other illustrations can be given to justify the form of M_8, but perhaps further explanation, if needed, is better sought in student exercises later.

An alternate form of the integral equation above is this differential equation:

$$\frac{dM_8}{dt} = \frac{k_r F_r - k_d F_d}{M_{5,\text{ref}}} \quad \text{with initial condition } M_8(1850) = 1 \tag{8}$$

The numerical value of the coefficient k_{15} in Eq. (6) can be calculated from the reference values shown in Figure 1, given values for Γ and γ and taking $M_8 = 1$ (its initial state).

With Eq. (8) added to the material balance equations, the complete mathematical model consists of the following set of eight ordinary differential equations:

$$\left.\begin{aligned}
\frac{dM_1}{dt} &= -\left(k_{12}+k_{13}\right)M_1 - k_{15}M_8\frac{M_1-\gamma}{M_1+\Gamma} + k_{21}M_2^{\beta_2} \\
&\quad + k_{31}M_3^{\beta_3} + k_{51}M_5 + k_{61}M_6 + F_f(t) + F_d(t) - F_r(t) \\
\frac{dM_2}{dt} &= k_{12}M_1 - \left(k_{23}+k_{24}\right)M_2 - k_{21}M_2^{\beta_2} + k_{42}M_4 \\
\frac{dM_3}{dt} &= k_{13}M_1 + k_{23}M_2 - k_{34}M_3 - k_{31}M_3^{\beta_3} + k_{43}M_4 \\
\frac{dM_4}{dt} &= k_{24}M_2 + k_{34}M_3 - \left(k_{42}+k_{43}\right)M_4 \\
\frac{dM_5}{dt} &= k_{15}M_8\frac{M_1-\gamma}{M_1+\Gamma} - \left(k_{51}+k_{56}\right)M_5 - F_d(t) + F_r(t) \\
\frac{dM_6}{dt} &= k_{56}M_5 - k_{61}M_6 \\
\frac{dM_7}{dt} &= -F_f(t) \\
\frac{dM_8}{dt} &= {-\left[k_dF_d(t) - k_rF_r(t)\right]}\Big/{M_{5,\mathrm{ref}}}
\end{aligned}\right\} \qquad (9)$$

Numerical values for the constants are given in Table 1. Determining the values of the k's, as described earlier, calibrates the model to the data for the reference year 1850. The value for γ is taken from Lenton's model. The value for k_d is somewhat arbitrary and could be adjusted by tuning the model, but I have taken it to be constant throughout at 0.23. (Lenton used a value of 0.27.) I have arbitrarily chosen a value of unity for k_r. My method for determining the value for Γ, the only tuning parameter, will be described in the next section. The values for β_2 and β_3 were determined as described earlier.

Implicit in this development is the assumption that the carbon cycle is independent of all other state variables, or that all others are constant, such as temperature, moisture, and other nutrient levels. That assumption is frequently invoked, but it may be an oversimplification if the model results are to be applied to global climate dynamics, for example. In the aforementioned work of Lenton[3] the carbon cycle is coupled to the Earth's energy balance, and in that of Ver *et al.*[7] to other nutrient cycles.

TUNING AND TESTING WITH HISTORICAL DATA

Extensive historical records are available for testing and tuning the model. Figure 2 shows data on emissions due to fossil fuel consumption, F_f, taken from Marland et al.,[11] and deforestation, F_d, taken from Houghton and Hackler,[12] as well as the total of the two over the period 1850 through 1990. (I used 1990 as the endpoint because the deforestation data given by Houghton and Hackler are not tabulated beyond that year. We can safely assume that reforestation, F_r, has been negligibly small in the past.) The dramatic increase in fossil fuel emissions since the middle of the twentieth century is evident.

The solid curves in Figure 2 show my empirical fit of the reported data. In order to get a rather precise representation I used separate functions over four segments of F_f and over six segments of F_d. This detailed fitting may seem to be overkill. I simply wanted to eliminate an inaccurate

TABLE 1

Numerical Values and Units for Model Constants

symbol	value	units
k_{12}	0.0931	y^{-1}
k_{13}	0.0311	y^{-1}
k_{15}	147	y^{-1}
k_{21}	$58(730^{-\beta_2})$	$PgC^{(1-\beta_2)}y^{-1}$
k_{23}	0.0781	y^{-1}
k_{24}	0.0164	y^{-1}
k_{31}	$18(140^{-\beta_3})$	$PgC^{(1-\beta_3)}y^{-1}$
k_{34}	0.714	y^{-1}
k_{42}	0.00189	y^{-1}
k_{43}	0.00114	y^{-1}
k_{51}	0.0862	y^{-1}
k_{56}	0.0862	y^{-1}
k_{61}	0.0333	y^{-1}
β_2	9.4	
β_3	10.2	
γ	62.0	PgC
Γ	198	PgC
k_d	0.230	
k_r	1.0	

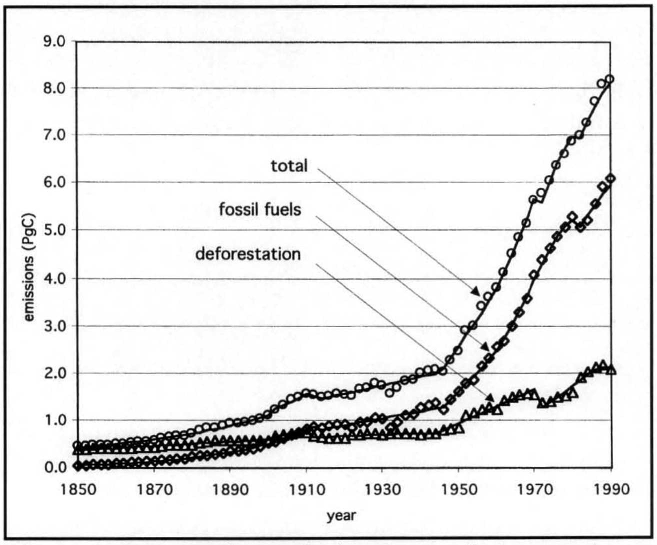

Figure 2. *Historical record of carbon emissions to the atmosphere. Symbols represent reported data;[11,12] solid curves are empirical fits.*

representation of the disturbance record as an explanation for any model failure.

With this representation of the historical disturbances and the model constants in Table 1, the system of ordinary differential equations in Eq. (10) can be solved readily, by numerical routines available in a number of software packages, to obtain a model-generated record of carbon in the reservoirs from 1850 through 1990. (I used Mathcad for this particular exercise and extensively throughout the course.) The solid curve of Figure 3 shows the result for atmospheric CO_2; the data points are reported estimates or measurements from the Worldwatch Institute database.[13] The good agreement between model results and reported data was assured over a portion of the curve, at least by my method of determining the value of Γ. Its value of 198 PgC, as given in Table 1, was determined by an iterative search aimed at minimizing the total squared difference between model results and reported data over the period 1980-1990. Admittedly, the good agreement over the early years was also virtually assured because model constants were calculated to give a perfect fit of the reference data of 1850. Over the other years, the maximum disagreement, which occurs around 1925, is less than 1.3%. All such things considered, this test of the model lends legitimacy to its use in predicting carbon distributions through some years ahead.

TABLE 2

Model Computed Quantities for 1990

i	M_i^*
1	753
2	744
3	143
4	37071
5	577
6	1489
7	5086
8	0.952

*Units of M_i are PgC, except M_8, which has no units.

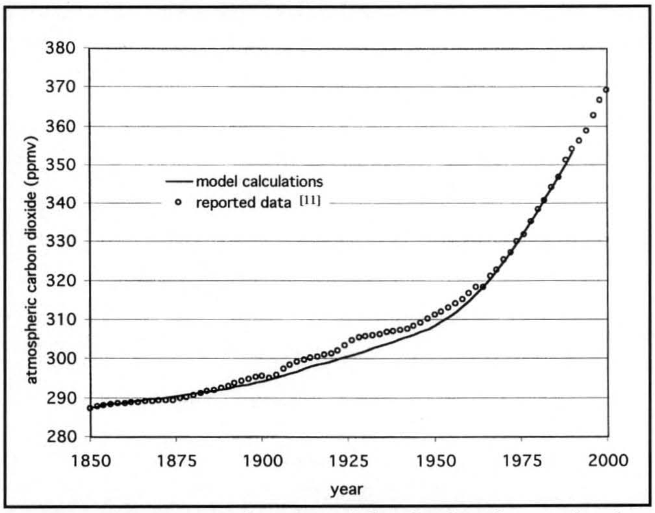

Figure 3. *Reported and model-calculated records of atmospheric carbon dioxide since 1850.*

Table 2 lists the calculated 1990 levels of carbon for all reservoirs. Notice that changes in the five of the six reservoirs have been relatively small over the 140-year period, according to the model. The terrestrial biota in box 5 increased only from 577 to 580 PgC owing to the offsetting effects of decreases by deforestation and increases by atmospheric CO_2 fertilization. The atmospheric reservoir increased by 23% by 1990 and is obviously destined to go higher, but changes in others have amounted to about 2% or less.

A total of 214 petagrams of new carbon was injected into the cycle from the fossil fuel reservoir and distributed among the other reservoirs over the period 1850 through 1990. Eventually most of that will reside in the deep oceans, box 4, but by 1990 that reservoir has increased by only 71 petagrams. Atmospheric carbon increased by 141 petagrams. Some of that redistribution of carbon, but not any of the increase in the total, is due to deforestation with a nonzero value of k_d.

In the simulations to follow, the ending values of the M's for 1990, given in Table 2, are used as the initial state.

SIMULATIONS

The simulations described in this section engage the students in the use of the model and exhort them to learn about current trends, issues, and possible future actions—and to become informed about likely consequences regarding future disturbances to the carbon cycle. The principal interest is in the prediction of atmospheric carbon dioxide levels through the 21st century. Such predictions, based on models of varying degrees of complexity, have been reported in a number of recent studies.[1,3,5,7,14]*

Disturbance Scenarios

Postulated scenarios for future carbon emissions over a century of time when human activities, worldwide economies, and international politics are involved are naturally laden with uncertainty, the effects of which, in fact, probably overshadow the effects of the assumptions and simplifications in the model itself. Notwithstanding such, predictions through simulations require inserting the disturbance functions F_f, F_d, and F_r into the model equations.

The most commonly employed scenarios for carbon emissions are those in a set of five that were suggested in a 1992 report to the International Panel on Climate Change, IPCC.[3,15]

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* *The list given in the References section is only a small sample. The interested reader will be led to a much larger assortment of models and related subjects simply by entering the keyword "carbon" on a web browser.*

Known by the names IS92a, IS92b, . . .IS92e, they are based on likely or possible trends in population changes, economic growth, energy supplies, etc. in developed and developing countries. There is also a Kyoto protocol, which, if enacted according to Article 3 of the agreement, would call for a worldwide decrease in emissions to 95% of the 1990 level by the year 2012.[16]

Shown in Figure 4 are slightly modified versions of three of the IS92 scenarios for total carbon emissions for 1990 onward, including the most pessimistic (IS92e) and the most optimistic (IS92c) cases, and what's usually referred to as the "business-as-usual" scenario (IS92a).[*] The latter is the most commonly used version, and as its description implies, is based on the assumption that carbon emissions can be predicted from current trends with no major changes in policies and practices.

Also shown in Figure 4 is a representation of the scenario for the Kyoto protocol, based on the assumption that emissions would be held constant after 2012. (Ver, *et al.*, used a similar representation.[7]) The IS92 scenarios break down the anticipated emissions into fossil fuel use and deforestation. All of them use the same deforestation pattern, which declines to zero by 2100. A curve showing the modified deforestation scenario is also included in Figure 4. The differences between that curve and the others in the figure are the fossil fuel components. Reforestation is not included in the scenarios as a separate disturbance.

Some Results

I use two different approaches for simulations, each having certain advantages over the other. One is a straightforward numerical solution of the differential equations using Mathcad—basically similar to the method used to generate the historical curve in Figure 3. It's the workhorse that I incorporate into classroom presentations and the major tool used by the students for assigned work. I constructed the other using LabVIEW®[**] to give a convenient user interface, a virtual laboratory, for certain classroom demonstrations and student experiments. It provides the user with hands-on control of the disturbances during a simulation, showing effects of manipulations "live" on virtual strip-chart recorders and digital displays. (Actually, I've used the LabVIEW simulation for classroom demonstration at the very beginning of the module because it is illustrative and serves to introduce goals and whet the appetite for learning about model development and simulations.) Space limitations prohibit a full description of the LabVIEW simulator and its operation here, but the gist of it is shown in the photo of the user's panel in Figure 5 and the brief description in the caption. Notice that those features afford the user an option of sequestering carbon by reforestation and by capturing a fraction of emissions, F_r, in the deep ocean and geologic reservoirs.

Figure 6 presents an example of the results of Mathcad simulations using the four scenarios of Figure 4. (For those simulations, I used linear interpolation between the data points shown in Figure 4 for the period 1990-2100.) The results in Figure 6 are based on the parameters listed in Table I except that here the values used for β_2 and β_3 are 11.0 and 12.3, respectively. (As I mentioned above, those values depend on the total carbon in the surface ocean reservoirs. I used the 1990 values of M_2 and M_3 given in Table 2 as a basis for the new β values for the period 1990-2100.) F_r is taken to be zero.

Notice that the model predicts atmospheric CO_2 would increase to 702 ppmv by the year 2100 if the IS92a *business-as-usual* scenario were followed. Based on that scenario, predictions by models used by others[1,3,14] range between 697 and 724 ppmv. Over the entire 110-year period, the maximum difference in atmospheric CO_2 between any two of the four models (the three cited above and the present one) is about 4%, an observation that buttresses confidence in discussions of quantitative results from the model at hand. Notice the wide range of predicted CO_2 levels in 2100 resulting from the different scenarios for carbon emissions. The highest is nearly twice the lowest; both are probably unrealistic extremes. Business-as-usual would result in nearly doubling the 1990 CO_2 level by the year 2100, according to the model prediction.

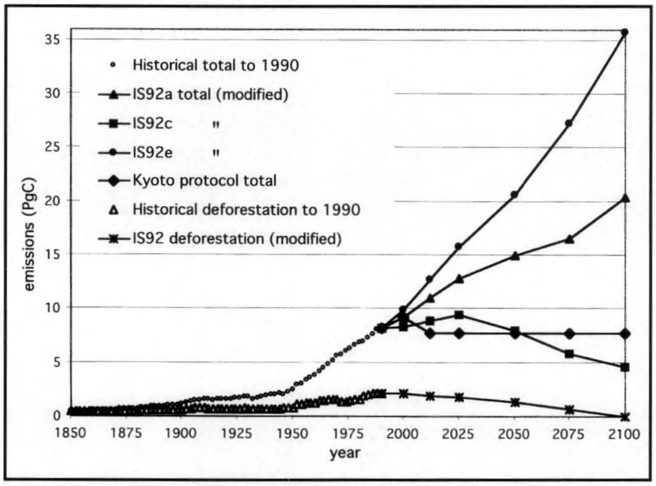

Figure 4. *Carbon emissions to the atmosphere; historical data and possible future scenarios.*

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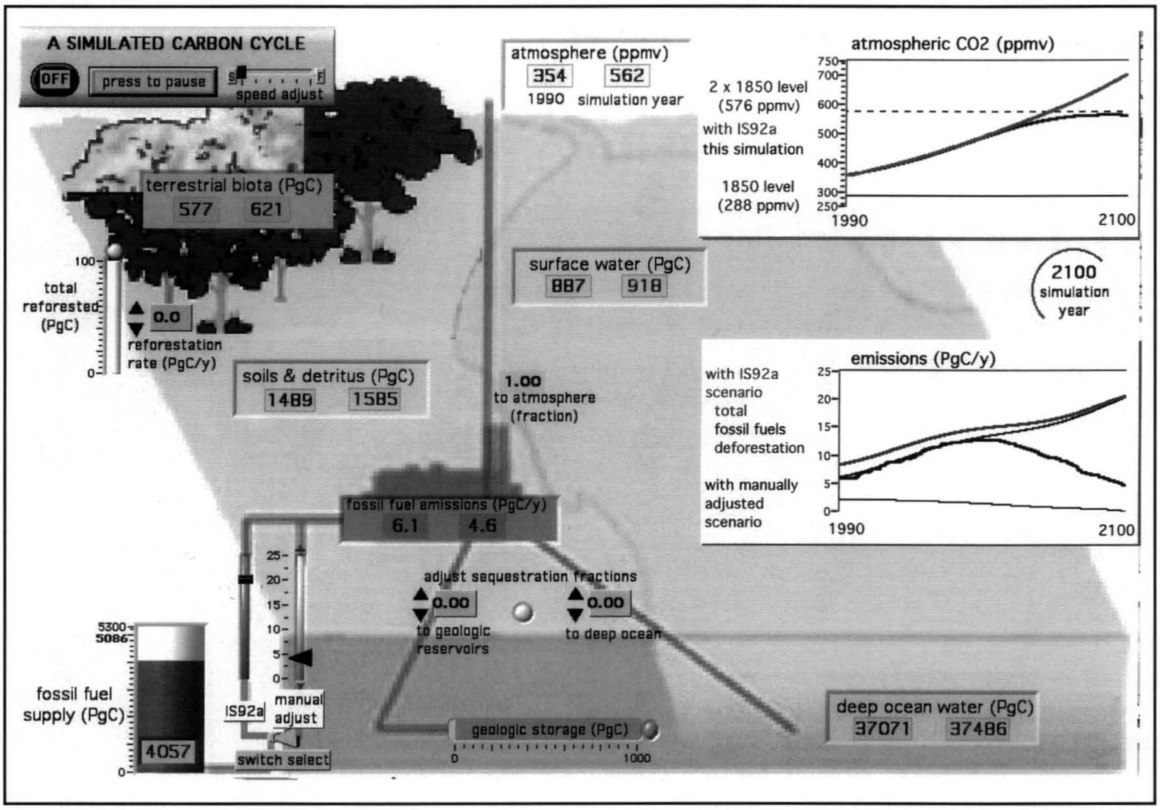
[*] *I modified the IS92 scenarios for both the fossil fuel and deforestation components in order to bring the 1990 values of the scenarios in agreement with the data actually reported for that year.*[11,12] *This amounted to adding 0.1 PgC to all of the IS92 fossil fuel quantities and increasing all of the deforestation values by about 50%. These modifications are more for refinement and fastidiousness than for any significant effect on calculations.*

[**] *LabVIEW, developed by the National Instruments Corporation in Austin, Texas, is graphical programming software developed mainly for data acquisition and instrument control. It also serves as a powerful tool for constructing virtual laboratories.*



A SIMULATED CARBON CYCLE

OFF | press to pause | speed adjust

atmosphere (ppmv): 354 | 562

1990 simulation year

terrestrial biota (PgC): 577 | 621

total reforested (PgC)

reforestation rate (PgC/y): 0.0

soils & detritus (PgC): 1489 | 1585

surface water (PgC): 887 | 918

1.00 to atmosphere (fraction)

fossil fuel emissions (PgC/y): 6.1 | 4.6

adjust sequestration fractions: 0.00 to geologic reservoirs | 0.00 to deep ocean

fossil fuel supply (PgC): 4057

IS92a | manual adjust | switch select

geologic storage (PgC)

deep ocean water (PgC): 37071 | 37486

2100 simulation year

Figure 5. *The user's panel for LabVIEW simulations. The elements with black arrows are for user inputs, adjustable as the simulation proceeds.*

The number to the left in each reservoir box is the initial value given in Table 2; that on the right, the current value.

The two surface water boxes of Figure 1 are combined into one for these simulations.

Additional Work

Using Mathcad and LabVIEW simulations, students obviously can be involved in examining all sorts of questions, model variations, and parameter effects. Here is a partial list of exercises that I have used, some of which require consulting outside references.

- Extend simulations beyond 2100 to address a number of questions raised about the ultimate steady state. (Actually, I ask the students to use the steady-state forms of the equations to address some of these.) What would that ultimate state be if emissions were halted immediately? What would it be if all carbon in the fossil fuel reservoir were eventually used? How long will it take to approach a steady state if carbon emissions to the atmosphere are halted at a certain time?

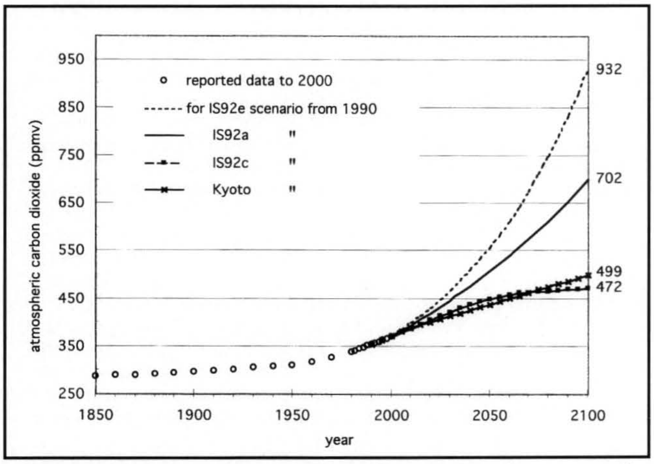


Figure 6. *Atmospheric carbon dioxide levels; reported historical data and model predictions.*

- Carry out simulations to clarify, if necessary, the roles and effects of k_d, k_r, and M_8—or to test entirely different forms of F_{15}, the rate of photosynthetic uptake of carbon.
- What is a realistic mathematical description for the disturbance, F_r, if reforestation begins with new trees that require a number of years for maturation?
- Examine the predicted changes in the strengths of the terrestrial and oceanic sinks (or sources?) of atmospheric carbon over the 21st century.
- It is sometimes suggested that the most realistic goal that can be achieved regarding the control of atmospheric CO_2 is to "stabilize" it at twice the pre-industrial level by the year 2100. Try to achieve that goal by manipulating the emissions (or by fabricating an emissions scenario) in such a way that atmospheric CO_2 lines out at about 1224 PgC (572 ppmv) by the year 2100. (This is an ideal exercise—even an entertaining one—for the LabVIEW simulator. In fact, the data shown on the digital displays and charts in Figure 5 are the end states of this exercise.) Notice that the difference between the emissions level so achieved in 2100 and that dictated by the IS92a sce-

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The Earth's Carbon Cycle

Continued from page 303.

nario (*i.e.*, the difference between the end points of curves of the lower strip chart of Figure 5) is the amount of carbon that would have to be replaced by an equivalent energy source. Follow-up questions for consideration and/or further simulations: *What alternate sources of energy might fill the gap? Could it be filled by sequestering carbon in the terrestrial biota (reforestation activities)? ...in geologic storage? ...in the deep ocean waters? Would those possibilities lead to a permanent stabilization? What is the trend of the fabricated emissions curve in 2100? What is its ultimate fate if atmospheric* CO_2 *is to stay level at 572 ppmv?*

- Start from the beginning with an alternative model that presumably improves on this one (*e.g.*, by adding layers to the ocean or atmosphere, a spatial variation to the terrestrial reservoirs). Calibrate, tune, and test the model against the results shown here.

CONCLUDING COMMENTS

Many of the Earth's biogeochemical processes can be studied and modeled within the context of the usual chemical engineering curricular material. The carbon cycle, the focus of this article, is a particularly apt example because, though basically complex, it can be usefully described by a simple mathematical model. Additionally, it is being disturbed and altered by human activities, possibly to the extent of causing global warming and other climate changes, and is therefore a subject of current interest and concern.

Aside from students learning about this particular subject, important and timely as it is, in my view another worthwhile outcome is that they gain confidence in their ability to analyze physical situations that may not be on their usual bill-of-fare and to apply their chemical engineering tools to the formation of a mathematical description. Never mind that the description is soaked with simplifications and assumptions—such as perfectly mixed boxes for oceans, single-rate expressions for all of the Earth's photosynthesis, and so on. A great deal is learned by pondering, investigating, and debating the bases for such simplifications and assumptions.

This article describes my coverage of the subject in a course devoted to topics on ecology and the environment. The coverage is scalable—downward to a brief treatment and selected homework assignments integrated into some of the usual core course offerings, or upward to the development of more sophisticated models and the application of more advanced descriptions of the rate processes, mathematical analysis, and computational methods. Whatever the scope, students benefit from the broadening experience of applying their chemical engineering tools in a quantitative way to an important subject outside the mainstream.

Readers who would like to have an electronic copy of this module, which consists of a slide show with links to spreadsheets, simulations, etc., including the LabVIEW simulator, should contact me at <schmitz.1@nd.edu>.

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