INTRODUCTION TO BIOGEOCHEMICAL CYCLES
Material Balances for Carbon

Introduction

Many of the earth's natural processes are cyclic. The circulation of water between oceans, atmosphere and continents is a familiar example. Another is the transformation and movement of carbon-containing compounds for which the immediately obvious elements are the photosynthetic generation by plants of carbohydrates from carbon dioxide and the consumption of carbohydrates by herbivores who regenerate carbon dioxide through respiration. (As we shall see shortly, the complete carbon cycle involves a number of additional processes.) Such cycles are termed "biogeochemical cycles." The term is most commonly used to refer to global cycles of the "life elements" C, O, N, S, and P, but its use is extended as well to regional cycles and to other elements or components.

The study of biogeochemical cycles then is the study of the transformation and transport of substances in the Earth's systems. In most cases the cycles link biotic (living) subsystems to abiotic (non-living) ones. Of particular current interest is the effect of human-caused disturbances on the natural cycles. A major disturbance in the carbon cycle, for example, is the continuous injection of carbon (mainly as carbon dioxide) into the atmosphere by the burning of fossil fuels. How much of this injected carbon ends up in the atmosphere? How much in the oceans? . . . in the land vegetation? What effect does the increase in carbon dioxide in the atmosphere have on the global climate? Insights to the answers to these and related questions can be gained through the use of mathematical models constructed by applying material and energy balance principles.

Here the carbon cycle serves as an illustrative example, though much of the discussion is couched in terms that apply generally. The objective is to develop a simple mathematical model that will demonstrate the use of material and energy balances for studying the Earth's natural processes.
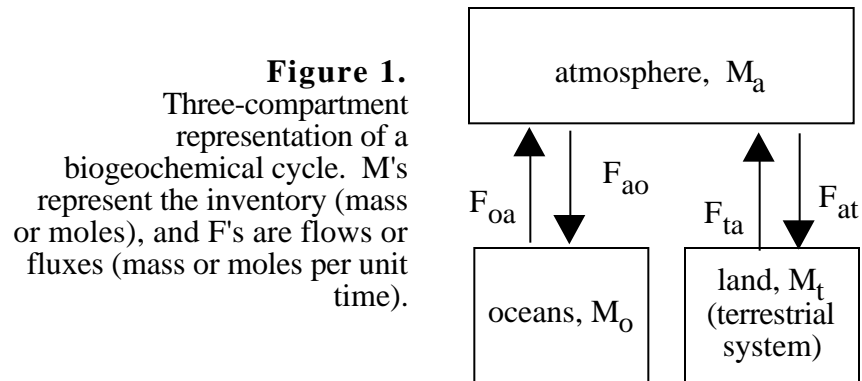
A schematic representation

The transport of substances in biogeochemical systems is commonly depicted graphically by means of flowsheets or flowcharts, which are composed of boxes (or compartments, or reservoirs) connected by arrow-directed lines. As such, the depiction resembles the flowsheet for a chemical plant or process where boxes represent various

units (reactors, heat exchangers, etc.) and the lines represent material flows. Indeed the analogy extends to methods of analysis, as we shall see in later sections, based on material and/or energy balances. Flowcharts for biogeochemical systems differ from those generally used for chemical processes in that a single chart for the former usually is used to track the flow of just one substance (ordinarily an element such as carbon) -- but it need not be so.

The number of boxes in a schematic representation is indicative of the level of detail to which an analysis will be subjected or for which information (data) is available. The least detailed for global carbon, for example, consists of only three compartments -- for land, oceans and atmosphere -- of the type shown in Figure 1.

Commonly in such representations, the amounts, or inventory, of the substance of interest (represented by M's in Figure 1) in each compartment have units of mass or moles. The exchange rates or flows (usually termed "fluxes" in the ecosystem literature, represented by F's in Figure 1) have units of mass or moles per unit of time.

Figure 1. Three-compartment representation of a biogeochemical cycle. M's represent the inventory (mass or moles), and F's are flows or fluxes (mass or moles per unit time).

A quantitative description would give numerical values of the inventories and fluxes -- or better yet, would give expressions for the F's in terms of the M's.

Figure 2 presents a similar flowchart with a slightly higher level of detail. This representation recognizes that there may be a significant difference between concentrations near the ocean surface and those in the deeper ocean layers. We will use this representation later for studying a model of the carbon cycle.

Figure 2. Four-compartment representation of a biogeochemical cycle.
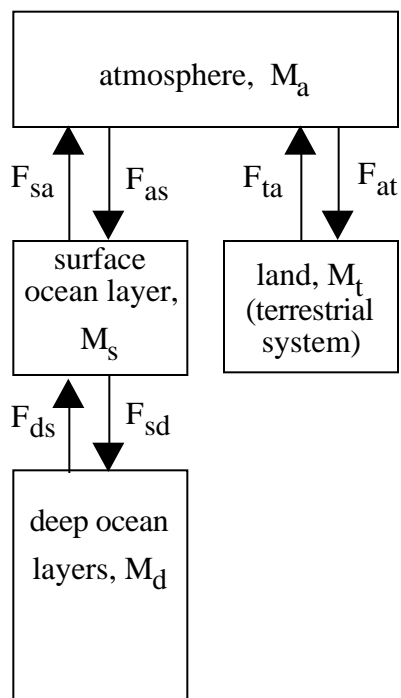
A further level of detail might add boxes to represent land and ocean biota, but we will not add that complexity for our purposes here.

Mathematical models

Mathematical models of biogeochemical cycles can take on various forms depending on the level of detail sought or necessary and/or on the type of supporting or verifying information or data available. In general, models attempt to relate the rates of transport, transformation and input of substances to their masses and changes by way of equations based on material and/or energy conservation principles.

The description in the preceding section suggests so-called "lumped" models; that is, models in which the spatial position is not a continuous variable. Indeed it may not even appear in the model equations. It is, in fact, considered to be piecewise constant. Thus the vertical position in the ocean was separated into two parts, surface layer and deep layers. For such lumped models, the mathematical description is in the form of ordinary differential equations for the unsteady states and of algebraic or transcendental equations for the steady state. So-called "distributed" models, which consider the spatial position to be a continuous variable, lead to partial differential equations for the unsteady and ordinary differential equations for the steady state. By far the most common models employed for biogeochemical cycles are of the lumped variety, and the remainder of this module will be devoted to them. One should think of lumped models as representing overall (perhaps

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global) averages. With sufficient detail (large number of boxes) they may be useful for accurate quantitative purposes; with little detail, they may be used to obtain rough estimates, to study qualitative trends, and to gain insights into the effects of changes.

Lumped models are sometimes referred to as "black box" models -- so called because they consider only the inputs and outputs of the boxes and their interior masses. They do not explore the interior details of the boxes -- such as the predator-prey interactions that influence the population dynamics within the biota, or the complex ocean chemistry that affects the air-ocean exchange of material. In the same way, most flowsheet representations and calculations for chemical plants treat process units as black boxes. Material and energy balances relate known and unknown stream quantities. The detail within a box, such as the tray-to-tray compositions and temperatures of a distillation column are not directly involved in the usual flowsheet calculation, but obviously are involved in determining the output streams, or in relating them to other streams, at a finer level of detail

Calculations for a model of the carbon cycle

Here we will use a schematic diagram similar to that in Figure 2 to construct a mathematical model for the carbon cycle. Our purpose is to estimate the effect of fossil fuel burning on the level of carbon in the atmosphere -- important information for the assessment of the greenhouse effect. Figure 2 is reconstructed below to include the input of carbon from fossil fuels.

Figure 3.
A simplified representation of the carbon cycle, including an input from fossil fuel burning.
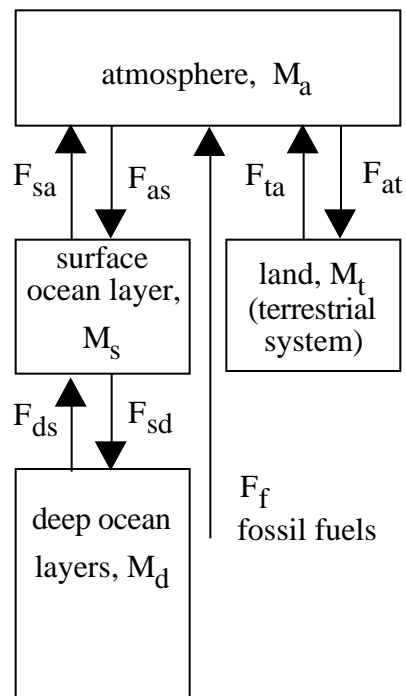
The following equations relate the flow rates (fluxes) in the diagram to the masses of carbon in the boxes in the form employed in references [1] and [2]. The numerical values of the coefficients were derived from data presented in those references. F_{fa} is an input disturbance, yet to be specified. In these equations, the masses (the M's) are in units of *petagrams*, and the fluxes (the F's) are in units of *petagrams per year*. (One petagram is 10^{15} grams.)

$$F_{as} = (0.143)M_a \tag{1}$$

$$F_{sa} = (10^{-25})M_s^{9.0} \tag{2}$$

$$F_{at} = (16.2)M_a^{0.2} \tag{3}$$

$$F_{ta} = (0.0200)M_t \tag{4}$$

$$F_{ds} = (0.00129)M_d \tag{5}$$

$$F_{sd} = (0.450)M_s \tag{6}$$

Notice that Equations 2 and 3 are nonlinear relationships between fluxes and masses. To appreciate the reason for this, say in Equation 2, bear in mind that the fluxes and masses are measures of the <u>element</u> C, which actually exists in various compound forms, with equilibrium likely established among them, in the ocean waters. Yet it is only carbon dioxide that enters the atmosphere from the ocean layers in any appreciable quantity. Therefore, the relationship between carbon dioxide and the total carbon in the ocean layers is complicated.

The nonlinear relationship in Equation 3 is explained by the fact that this rate of transfer, nearly all in the form of carbon dioxide, is governed mainly by the rate of photosynthesis by plants -- a rate usually not limited by carbon dioxide supply from the air but rather by the photochemical and biochemical reactions at play.

Material balances

Material balances on carbon (i.e., atomic balances) may be written for each of the boxes in Figure 3. As an example, with the information in Equations 1-6 incorporated, the unsteady balance on the "atmosphere" box is given by

$$\frac{dM_a}{dt} = \left(10^{-25}\right) M_s^{9.0} + \left(0.0200\right) M_t - \left(0.143\right) M_a - \left(16.2\right) M_a^{0.2} + F_f \qquad (7)$$

Similar balances must be added for the other three compartments, and initial values for the four M's must be given to complete the mathematical model. The input from fossil fuel consumption, the disturbance function F_f, may be a constant or a function of time. Its current value is about 5 petagrams of carbon per year. Over some periods of time its value increased at the rate of about 4% per year. Inasmuch as the Earth's total reservoir of fossil fuels is estimated to be 10,000 petagrams, of which only half may be recoverable for use, the current use rate, much less any significant increase, is not sustainable indefinitely. However, in the much shorter run, the concern is not about the availability of fossil fuels, but about how their use may be affecting the global climate.

Steady states. The steady-state model is derived simply by setting the time derivatives in the transient equations to zero. Further, we can deduce from physical considerations that no steady state is possible unless F_f is zero. (Notice that the steady-state equations are nonlinear in the M's owing to the exponents on M_s and M_a. Consequently, a numerical search procedure must be used to obtain solutions to Problem 1 below.)

Problem 1

Incorporating the information in Equations 1-6, write the steady-state carbon balance for each of the four "boxes" in Figure 3, taking F_f to be zero. Can you solve these equations for the numerical values of the four M's? (Note that the equations are not linearly independent; one is redundant.)

(a) Take the total M (i.e., the sum of the four M's) to be 39,700 petagrams (the actual current estimate of the total carbon in the four compartments) and solve for the M's. Note that your solution would be the ultimate steady-state distribution of carbon if the usage of fossil fuels were discontinued now -- that is if F_f were immediately decreased from 5 petagrams per year to zero.

(b) Instead of assuming an immediate reduction in F_f to zero, suppose that the usage of fossil fuels is reduced gradually in such manner that the carbon entering the atmosphere from this source decreases linearly with

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time from 5 petagrams per year to zero over the next 100 years. Calculate the total amount (in petagrams) of carbon released by fossil fuel use over that 100-year period, and determine the new set of M's at steady state. What fraction of the added carbon will ultimately (steadily) reside in the atmosphere?

Unsteady (Transient) States. While information about steady states is of interest and importance, the more relevant questions can only be answered by examining the transient or unsteady state. How long does it take to approach a steady state? What levels of carbon are reached in the atmosphere along the way to an eventual steady state? What is the effect of increasing or decreasing the rate of consumption of fossil fuels?

Consider the first question. According to the numerical values given above for fluxes and reservoir levels of carbon, the effective time constants for the reservoirs vary from a few years for the atmosphere to hundreds or thousands of years for the deep ocean layers. Therefore, a large input into the atmosphere may eventually decay to only a modest permanent (steady-state) increase owing to the fact that the large capacity of the oceans will eventually absorb most of it -- but the effects on the atmosphere may be felt for a century or more.

The point was made above that the steady-state equations, being nonlinear, cannot be solved analytically. The same is true for the unsteady state. Therefore, the following problem requires a numerical procedure for solving the system of nonlinear ordinary differential equations.

Problem 2.

Equation 7 gives the material balance for carbon in the atmosphere. Complete the mathematical description of the unsteady state by writing similar balances on the remaining three compartments shown in Figure 3. Take the initial (current) levels of carbon in the four reservoirs to be 700, 3000, 1000, 35000 for the atmosphere, terrestrial, surface ocean, and deep ocean reservoirs, respectively -- all in petagrams.

(a) Assuming that the carbon input from fossil fuel use remains constant at its present level of 5 petagrams per year, generate a numerical solution giving the amount of carbon in each reservoir versus time over a 100-year period. (Show your results in graphical form.)

(b) As in part (b) of Problem 1, let F_f decrease linearly with time from 5 petagrams per year to zero over 100 years. Again generate solutions and present curves showing the

reservoir levels of carbon versus time up to 100 years. What fraction of the total carbon entering the atmosphere from fossil fuel use is present in the atmosphere at the end of the 100-year period? Compare that fraction to your answer for part (b) of Problem 1. Comments?

A Glance at the Global Warming Problem

You might ask why should we be concerned about changes in atmospheric carbon levels. After all, the levels are very low. Further, we should expect some natural level of CO_2 in the atmosphere owing simply to that generated by the respiration of plants and animals. In fact, that natural level is estimated to be about 280 ppmv -- a pre-industrial level that probably existed steadily for centuries before the industrial revolution. The answer to such questions is not simple, but the major concern nowadays is the possible upsetting of the Earth's energy balance leading to an increase in the average global temperature. We will not attempt an exhaustive treatment of this subject here, but since it connects directly to the preceding discussion of the carbon cycle, it warrants a quick glance at least.

The following equation gives the simplest form of the Earth's energy balance.

$$S(1 - f)\pi r^2 = \varepsilon \sigma T^4 (4\pi r^2) \tag{8}$$

where

S is the solar constant -- i.e., the amount of incident solar radiation per unit projected area of the Earth,

f is the albedo or reflectivity of the Earth,

r is the Earth's radius

is the effective emissivity of the Earth for infrared radiation to outer space,

is the Stefan-Boltzmann constant

T is the absolute temperature -- indicative of the global average temperature.

The radius, r, cancels from Equation 8. The following list gives values for the other quantities in Equation 8.

$S = 1367$ watts/m^2

$f = 0.31$

$= 0.615$

$= 5.5597 \times 10^{-8}$ watts/(m^2 $°K^4$)

Equation 8 is a steady-state balance equating the solar energy reaching the Earth's surface (on the left side) to the energy lost by infrared radiation to outer space (on the right side). Atmospheric gases affect the reflectivity, f, and the effective emissivity, . In particular, so-called *greenhouse* gases decrease by absorbing, or "trapping", some of the infrared radiation, thereby reducing the amount of energy that can escape from the Earth. If all other factors are constant, a lower value of will result in a higher value of T from Equation 8. Other factors come into the picture, however, and lead to uncertainty about the extent of global warming that may occur due to increases in CO_2 and other greenhouse gases. For example, an increase in the average temperature would probably lead to an increase in aerosols and cloudiness, which will act to increase f and offset the effect of a decrease in . We probably error on the pessimistic side (i.e., predicting a temperature change that is too large) if we assume, as we shall here, that an increasing CO_2 level works only to decrease . The following equation gives a reasonable estimate for that variation.

$$\varepsilon = 0.642 - (8.45 \text{ x } 10^{-5}) \, p_{co_2} \qquad\qquad (9)$$

where p_{CO2} is the concentration of carbon dioxide in the atmosphere in parts per million by volume (ppmv).

Problem 3

For this problem you will need to calculate the concentration of CO_2 in ppmv from the total mass of atmospheric carbon. For that calculation, take the total mass of the atmosphere to be $5.25 \text{ x } 10^{18}$ kg. In all cases use the initial values for the M's given in Problem 2.

(a) Using your result from Problem 1(b) along with Equations 8 and 9, calculate the predicted eventual increase in the global temperature attributable to the carbon added to the atmosphere over a 100-year period.

(b) Repeat Problems 2(a) and 2(b), this time including a graph of the global temperature change versus years as predicted from Equations 8 and 9. Comment about the resulting temperature following from Problem 2(b) vis-a`-vis that following from Problem 1(b).

Problem solutions

Solutions to the three problems presented in these notes are available to course instructors as Mathcad (Macintosh) files or as copies of those files in pdf format. Copies may be obtained by e-mail request to schmitz.1@nd.edu.

References

[1] Butcher, S. S., R. J. Charlson, G. H. Orians and G. V. Wolfe (Editors), *Global Biogeochemical Cycles*, Academic Press (1992)

[2] Rodhe, H. and A. Bjorkstrom, Some consequences of non-proportionality between fluxes and reservoir contents in natural systems, *Tellus* <u>31</u> 269-278 (1979)