

Modeling Biogeochemical Cycles

Henning Rodhe

4.1 Introductory Remarks

The chemical and physical status of the Earth is characterized by transport and transformation processes, many of which are of a cyclical nature. The circulation of water between oceans, atmosphere, and continents is an example of such a cyclic process. The basic characteristics of a cycle of a particular element or compound are often described in terms of the content in the various reservoirs and the fluxes between them. In our example, the reservoirs could be "the oceans", "the water in the atmosphere", "the ground water", etc. A fundamental question in the cycle approach is the determination of how the rates of transfer between the reservoirs depend on the content of the reservoirs and on other, external, factors. In many cases, the details of the distribution of the element within each of the reservoirs are disregarded.

The cycle approach to describe the physiochemical environment on Earth has advantages as well as disadvantages. The advantages include the following.

1. It provides an overview of fluxes, reservoir contents, and turnover times.
2. It gives a basis for quantitative modeling.
3. It helps to estimate the relative magnitudes of anthropogenic and natural fluxes.
4. It stimulates questions such as: Where is the material coming from? Where is it going next?
5. It helps to identify gaps in knowledge.

The following are some of the disadvantages.

1. The analysis is by necessity superficial. It pro-

vides little or no insight into what goes on inside the reservoirs or into the nature of the fluxes between them.

2. It gives a false impression of certainty. Very often, at least, one of the fluxes in a budget is derived from balance considerations. Such estimates may erroneously be taken to represent solid knowledge.
3. The analysis is based on averaged quantities that cannot always be easily measured because of spatial variation and other complicating factors.

Many important geophysical problems cannot be studied using the simplified cycle approach. Weather forecasting, for example, requires a detailed knowledge about the distribution of winds, temperature, etc., within the atmosphere. In this case, it is obviously not possible to use a reservoir model with the atmosphere as one of the reservoirs. It would not be much better even if one divided the atmosphere into a few reservoirs. A forecast model requires a resolution fine enough to resolve explicitly the structure of the most important weather phenomena such as cyclones, anticyclones, and wave patterns on spatial scales from a few hundred kilometers upwards. Models of this kind are based either on a division of the physical space into a large but finite number of grid cubes (grid point models) or on a separation of the variables into different wave numbers (spectral models). It is possible to look at such models as reservoir models consisting of very many reservoirs. However, this is normally not done.

The purpose of this chapter is to introduce and define the basic concepts used in the description and modeling of biogeochemical cycles. The last two

sections contain a brief summary of transport processes and the time-scales characterizing exchange processes in the atmosphere and oceans.

4.2 Reservoir Models and Cycles: Some Definitions

The following definitions are applicable to studies of biogeochemical cycles.

1. *Reservoir (box, compartment)*. An amount of material defined by certain physical, chemical, or biological characteristics that, under the particular consideration, can be considered as reasonably homogeneous. For example:

- oxygen in the atmosphere;
- carbon monoxide in the southern hemisphere;
- carbon in living organic matter in the ocean surface layer;
- ocean water having a density between ρ_1 and ρ_2 ;
- sulfur in sedimentary rocks.

In situations where the reservoir is defined by its physical boundaries, it is not uncommon to refer to its content of the specific element as its *burden*. We will denote the content of the reservoir by M . The dimension of M would normally be mass, although it could also be, for example, moles.

2. *Flux*. The amount of material transferred from one reservoir to another per unit time, in general denoted by F (mass per time). For example:

- the rate of evaporation of water from the ocean surface to the atmosphere;
- the rate of oxidation of N_2O in the stratosphere (i.e. flux from the atmospheric N_2O -nitrogen reservoir to the stratospheric NO_x -nitrogen reservoir);
- the rate of deposition of phosphorus on marine sediments.

In more specific studies of transport processes, the flux is normally defined as the amount of material transferred per unit area per unit time. To distinguish between these two conflicting usages, we shall refer to the latter as "flux density".

3. *Source*. A flux (Q) of material into a reservoir.

4. *Sink*. A flux (S) of material out of a reservoir. Very often this flux is assumed to be proportional to the content of the reservoir ($S = kM$). In such cases,

the sink flux is referred to as a first-order process. If the sink flux is constant, independent of the reservoir content, the process is of zero order. Higher-order fluxes, i.e. $S = kM^\alpha$ with $\alpha > 1$, also occur.

5. *Budget*. A balance sheet of all sources and sinks of a reservoir. If sources and sinks balance and do not change with time, the reservoir is in *steady-state*, i.e. M does not change with time. It is common in many budget estimates that some fluxes are better known than others. If steady-state prevails, a flux that is unknown *a priori* can be estimated by its difference from the other fluxes. If this is done, it should be made very clear in the presentation of the budget which of the fluxes is estimated as a difference.
6. *Turnover time*. The turnover time of a reservoir is the ratio of the content M of the reservoir to the sum of its sinks S or the ratio of M to the sources Q (see Section 4.3). The turnover time is the time it will take to empty the reservoir in the absence of sources if the sinks remain constant. It is also a measure of the average of the times spent by individual molecules or atoms in the reservoir (more about this in the next section).
7. *Cycle*. A system consisting of two or more connected reservoirs, where a large part of the material is transferred through the system in a cyclic fashion. If all material cycles *within* the system, the system is *closed*. In many situations, one may consider systems of connected reservoirs that are not cyclic but where material flows unidirectionally. In this connection, some reservoirs (at the end of the chain) may be *accumulative*, whereas others remain unbalanced (*non-accumulative*) (cf. Holland, 1978).
8. *Geochemical cycle*. In geology and geochemistry, the reservoirs and fluxes depicted in Fig. 4-1 are often referred to as the geochemical cycle. It might as well have been called the geophysiochemical cycle.
9. *Biogeochemical cycle*. This term is often used to describe the global or regional cycles of the "life elements" C, O, N, S, and P with reservoirs including the whole or part of the atmosphere, the ocean, the sediments, and the living organisms. Figure 4-2 shows the principal reservoirs and fluxes in the global biogeochemical carbon cycle as an example. The term can be applied to the corresponding cycles of other elements or compounds.

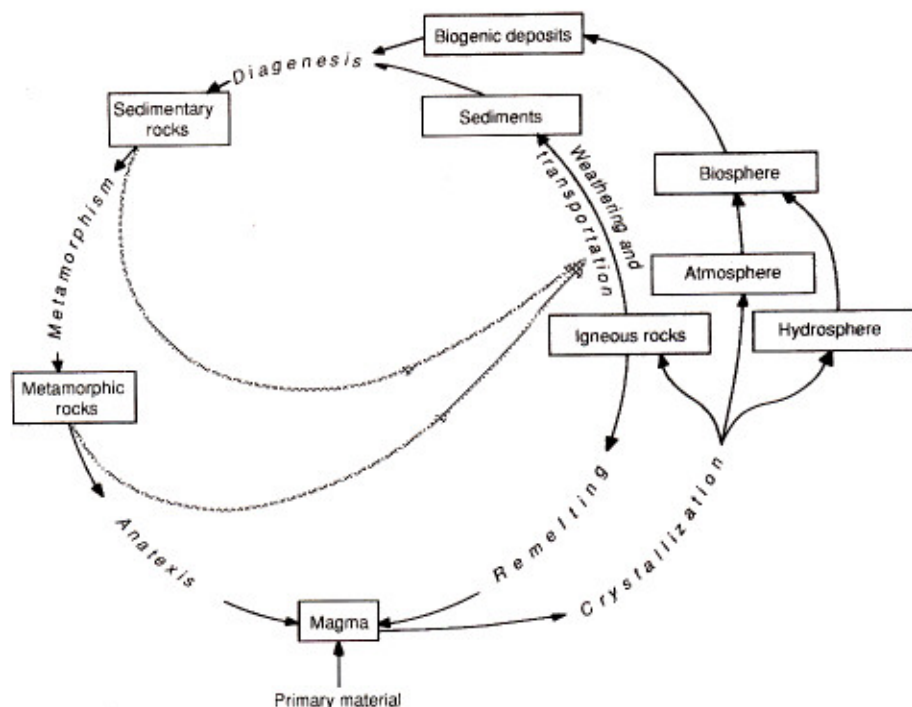


Fig. 4-1 The geochemical cycle showing the flux of material between various reservoirs in the geosphere. Adapted from Mason (1984) with the permission of John Wiley and Sons, Inc.

General comments

Budgets and cycles can be considered on very different *spatial scales*. In this book, we concentrate on global, hemispheric, and regional scales. The choice of a suitable scale (i.e. the size of the reservoirs) should be determined by the degree of ambition of the analysis as well as by the homogeneity of the spatial distribution. For example, in carbon cycle models it is reasonable to consider the atmosphere as one reservoir (the concentration of CO_2 in the atmosphere is fairly uniform). On the other hand, oceanic carbon content and carbon exchange processes exhibit large spatial variations and it is reasonable to separate the surface layer from the deeper layers, the Atlantic from the Pacific, etc. Many sulfur and nitrogen compounds in the atmosphere occur in very different concentrations in different regions of the world. For these compounds, regional budgets tell us more about the real situation at any one place than global budgets.

We shall in the main be concerned with processes that occur on *time-scales* longer than, or equal to, a season (3 months). This implies that we may consider the variables and the parameters of our models as time-averaged quantities with an averaging time of at least a season.

4.3 Time-scales and Single Reservoir Systems

4.3.1 Turnover Time

The turnover time is the ratio between the content (M) of a reservoir and the total flux out of it (S):

$$\tau_0 = M/S \quad (1)$$

The turnover time may be thought of as the time it would take to empty the reservoir if the sink (S) remained constant while the sources were zero ($\tau_0 S = M$). In fluid reservoirs like the atmosphere or

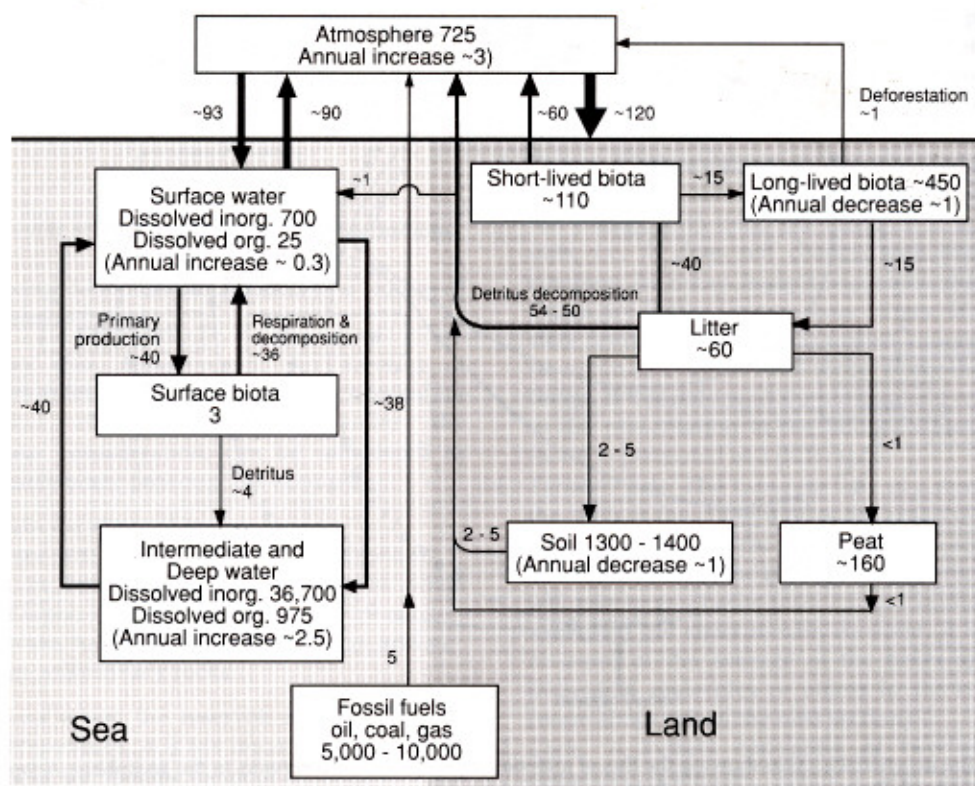


Fig. 4-2 Principal reservoirs and fluxes in the carbon cycle. Units are 10^{15} g C (burdens) and 10^{15} g C/year (fluxes). From Bolin (1986) with permission from John Wiley and Sons.

the ocean, the turnover time is also related to the spatial variability of the tracer concentration within the reservoir: a long turnover time corresponds to a small variability and vice versa (Junge, 1974; Hamrud, 1983).

If material is removed from the reservoir by two or more separate processes, each with a flux S_i , one can define turnover times with respect to each such process as:

$$\tau_{0i} = M/S_i \quad (2)$$

Since $\sum S_i = S$, these time-scales are related to the turnover time of the reservoir, τ_0 , by

$$\tau_0^{-1} = \sum \tau_{0i}^{-1} \quad (3)$$

The equation describing the rate of change of the content of a reservoir can be written as:

$$\frac{dM}{dt} = Q - S = Q - M/\tau_0 \quad (4)$$

If the reservoir is in steady-state ($dM/dt = 0$), sources (Q) and sinks (S) must balance. In this case, S can be replaced by Q in equation (1).

4.3.2 Residence Time (transit time)

The *residence time* is the time spent in a reservoir by an individual atom or molecule. It is also the age of a molecule when it leaves the reservoir. If the pathway of the atom from the source to the sink is characterized by a physical transport, the term *transit time* can be used as an alternative. Even for the same element (or compound), different atoms (or molecules) will have different residence times in a given reservoir. The probability density function of residence times is denoted by $\phi(\tau)$, where $\phi(\tau)d\tau$ describes the fraction of the atoms (molecules) having a residence time in the interval τ to $\tau + d\tau$. The probability density function may have very

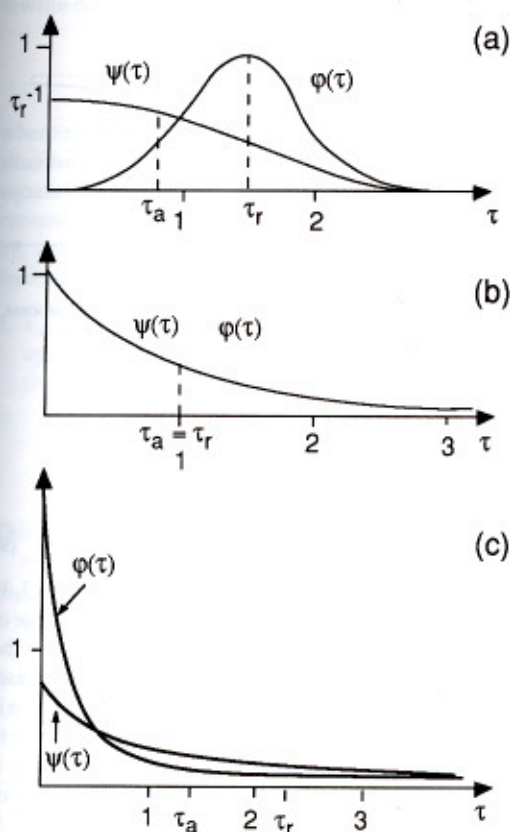


Fig. 4-3 The age frequency function $\psi(\tau)$ and the transit time frequency function $\phi(\tau)$ and the corresponding average age values τ_a and τ_r for the three cases described in the text: (a) $\tau_a < \tau_r$; (b) $\tau_a = \tau_r$; (c) $\tau_a > \tau_r$. Adapted from Bolin and Rodhe (1973) with the permission of the Swedish Geophysical Society, Stockholm.

different shapes. Some examples are shown in Fig. 4-3. This figure also contains the frequency function of age. These terms are further illustrated below.

Figure 4-3a might correspond to a lake with inlet and outlet on opposite sides of the lake. Most water molecules will then have a residence time in the lake roughly equal to the time it takes for the mean current to carry the water from the inlet to the outlet. Another example is a human population where most people live to a mature age. Figure 4-3b illustrates the common situation with exponential decay or with a well-mixed reservoir. A simple example could be the reservoir of all ^{238}U on Earth. The half-life of this nuclide is 4.5×10^9 years, implying that the content

of this reservoir today is about half of what it was when the planet Earth was formed 4.5 Ga ago. The probability density function of residence time of the uranium atoms originally present is an exponential decay function. The average residence time is 6.5×10^9 years. (The average value of time for an exponential decay function is the half-life divided by $\ln 2$.) In the reservoir corresponding to Fig. 4-3c, the removal is biased toward "young" particles. This might occur when the sink is located close to the source (the "short circuit" case).

The average residence time (average transit time) τ_r is defined by

$$\tau_r = \int_0^{\infty} \tau \phi(\tau) d\tau \quad (5)$$

In many cases, the word "average" is left out and this quantity is simply referred to as "residence time".

4.3.3 Age

The age of an atom or molecule in a reservoir is the time since it entered the reservoir. Age is defined for all molecules, whether they are leaving the reservoir or not. As with residence times, the probability density function of ages [$\psi(\tau)$] can have different shapes. In a steady-state reservoir, however, $\psi(\tau)$ is always a non-increasing function. The shapes of $\psi(\tau)$ corresponding to the three residence time distributions discussed above are included in Fig. 4-3.

The average age of atoms in a reservoir is given by:

$$\tau_a = \int_0^{\infty} \tau \psi(\tau) d\tau \quad (6)$$

4.3.4 Relations between τ_0 , τ_r and τ_a

For a reservoir in steady-state, τ_0 is equal to τ_r , i.e. the turnover time is equal to the average residence time spent in the reservoir by individual particles (Eriksson, 1971; Bolin and Rodhe, 1973).

This may seem to be a trivial result, but it is actually of great significance. For example, if τ_0 can be estimated from budget considerations by comparing fluxes and burdens and if the average transport velocity (V) within the reservoir is known, the average distance ($L = V\tau_r$) over which the transport takes place in the reservoir can be estimated.

The relation between τ_0 and τ_a is less simple. τ_a can be larger or less than τ_0 depending upon the shape of the age distribution (cf. Fig. 4-3). For a well-mixed reservoir, or one with a first-order removal process, $\tau_a = \tau_0$.

In the case of a human population (Fig. 4-3a), τ_a is only about half of τ_0 : the average age of all Swedes is between 35 and 40 years, whereas the average residence time, i.e. the average length of life (average age at death), is just over 70 years.

In the situation where most atoms leave the reservoir quickly but a few of them survive very long, τ_a is larger than τ_0 (the "short circuit" case). Some further examples of age distributions and relations between τ_a and τ_0 are given in Lerman (1979).

When equating τ_0 and τ_r , it must be made clear that the flux (S) defining τ_0 is the *gross* flux and not a net flux. For example, the removal of water from the atmosphere is brought about by both precipitation and dry deposition (direct uptake by diffusion to the surface). The dry deposition is normally not explicitly evaluated but subtracted from the gross evaporation flux to yield the net evaporation from the surface. The turnover time of water in the atmosphere calculated as the ratio between the atmospheric content and the precipitation rate (10 days) is thus *not* equal to the average residence time of water molecules in the atmosphere. The actual value of the average residence time of individual water molecules is substantially shorter.

4.3.5 Response Time

The response time of a reservoir is a time-scale that characterizes the adjustment to equilibrium after a sudden change in the system. A precise definition is not easy to give except in special circumstances as in the following example.

Consider a single reservoir for which the sink is proportional to the content ($S = kM$) and which is initially at equilibrium with fluxes $Q_0 = S_0$ and content M_0 . The turnover time of this reservoir is:

$$\tau_0 = M_0/S_0 = 1/k \quad (7)$$

Suppose now that the source strength is suddenly changed to a new value Q_1 . How long would it take for the reservoir to reach a new equilibrium? The adjustment process is described by the differential equation

$$\frac{dM}{dt} = Q_1 - S = Q_1 - kM \quad (8)$$

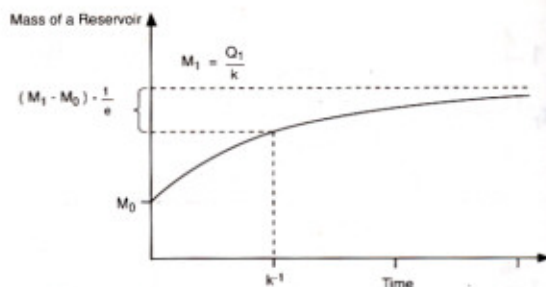


Fig. 4-4 Illustration of an exponential adjustment process. In this case, the response time is equal to k^{-1} .

with the initial condition $M(t=0) = M_0$.

The solution

$$M(t) = M_1 - (M_1 - M_0) \exp(-kt) \quad (9)$$

approaches the new equilibrium value ($M_1 = Q_1/k$) with a response time equal to k^{-1} or τ_0 . The change of the reservoir mass from the initial value M_0 to the final value M_1 is illustrated in Fig. 4-4. In this case, with an exponential adjustment, the response time is defined as the time it takes to reduce the imbalance to $e^{-1} = 37\%$ of the initial imbalance. This time-scale is sometimes referred to as "e-folding time". Thus, for a single reservoir with a sink proportional to its content, the response time equals the turnover time.

As a specific example, consider oceanic sulfate as the reservoir. Its main source is river run-off (pre-industrial value: 100 Tg S/year) and the sink is probably incorporation into the lithosphere by hydrogeothermal circulation in mid-ocean ridges (100 Tg S/year, McDuff and Morel, 1980; cf. Chapter 13). The content of sulfate in the oceans is about 1.3×10^9 Tg S. If we make the (unrealistic) assumption that the present run-off (200 Tg S/year) would continue indefinitely, how long would it take for the sulfate concentration in the ocean to adjust to this new flux? The answer is $\tau_0 \sim 1.3 \times 10^9 \text{ Tg} / 10^2 \text{ Tg/year} \sim 10^7$ years. A more detailed treatment of a similar problem can be found in Southam and Hay (1976).

4.3.6 Reservoirs in Non-steady-state

Let us analyze the situation when one observes a change in reservoir content and wants to draw conclusions regarding the sources and sinks. We

rewrite equation (8) as:

$$\frac{1}{M} \frac{dM}{dt} = \frac{Q}{M} - \frac{1}{\tau_0}$$

where $\tau_0 = 1/k$ is the turnover time in the steady-state situation. Let us denote the left-hand side of the equation (the observed rate of change of the reservoir content) by τ_{obs}^{-1} . If the mass is observed to increase by, say, 1% per year, τ_{obs} would be 100 years. Two limiting cases can be singled out:

1. $\tau_{\text{obs}} \gg \tau_0$. In this case, there has to be an approximate balance between the two terms on the right-hand side of the equation:

$$\frac{Q}{M} \approx \frac{1}{\tau_0} \text{ or } Q \approx \frac{M}{\tau_0}$$

This means that the observed change in M mainly reflects a change in the source flux Q or the sink function. As an example, we may take the methane concentration in the atmosphere, which is now increasing by about 1% per year. The turnover time is estimated to be about 10 years, i.e. much less than τ_{obs} of 100 years (Cicerone and Oremland, 1988). Consequently, the observed rate of increase in atmospheric methane is a direct consequence of a similar rate of increase of emissions into the atmosphere. (In fact, this is not quite true. A fraction of the observed increase is probably due to a decrease in sink strength caused by a decrease in the concentration of hydroxyl radicals responsible for the decomposition of methane in the atmosphere.)

2. $\tau_{\text{obs}} \ll \tau_0$. In this case, the balance is $dM/dt \approx Q$, which means that there is an increase in reservoir content about equal to the source flux with little influence of the sink. The reservoir is then in an accumulative stage and its mass is increasing with time largely as a function of Q . The content of CFC-12 in the atmosphere is an interesting example of this situation. The observed increase is about 4% per year ($\tau_{\text{obs}} \approx 25$ years) and the turnover time is about 120 years. The rate of increase is thus a reflection of an imbalance between sources and sinks rather than an increase in the source flux Q . The emissions of CFC-12 actually remained essentially constant between 1974 and 1988.

In situations where τ_{obs} is comparable in magnitude to τ_0 , a more complex relation prevails between Q , S , and M . Atmospheric CO_2 falls in

this last category, although its turnover time (3–4 years, cf. Fig. 4.2) is much shorter than τ_{obs} (about 300 years). This is because the atmospheric CO_2 reservoir is closely coupled to the carbon reservoir in the biota and in the surface layer of the oceans (Section 4.4). The effective turnover time of the combined system is actually several hundred years (Rodhe and Björkström, 1979).

4.4 Coupled Reservoirs

The treatment of time-scales and dynamic behavior of single reservoirs given in the previous section can easily be generalized to systems of two or more reservoirs. While the simple system analyzed in the previous section illustrates many important characteristics of cycles, most natural cycles are more complex. The matrix method described in Section 4.4.1 provides an approach to systems with very large numbers of reservoirs that is, at least, notationally simple. The treatments in the preceding section and in Section 4.4.1 are still limited to linear systems. In many cases, we assume linearity because our knowledge is not adequate to assume any other dependence and because the solution of linear systems is straightforward. There are, however, some important cases where non-linearities are reasonably well understood. A few of these cases are described in Section 4.4.2.

As important as coupled reservoirs and non-linear systems are, the less mathematically inclined may want to read this section only for its qualitative material. The treatment described here is not essential for understanding the reading later in the book.

4.4.1 Linear Systems

A linear system of reservoirs is one where the fluxes between the reservoirs is linearly related to the reservoir contents. A special case, that is commonly assumed to apply, is one where the fluxes between reservoirs are proportional to the content of the reservoirs where they originate. Under this proportionality assumption, the flux F_{ij} from reservoir i to reservoir j is given by:

$$F_{ij} = k_{ij} M_i \quad (10)$$

The rate of change of the amount M_i in reservoir i is

thus:

$$\frac{dM_i}{dt} = \sum_{j=1}^n k_{ji} M_j - M_i \sum_{j=1}^n k_{ij} \text{ for } j \neq i \quad (11)$$

where n is the total number of reservoirs in the system.

This system of differential equations can be written in matrix form as

$$\frac{d\mathbf{M}}{dt} = \mathbf{k}\mathbf{M} \quad (12)$$

where the vector \mathbf{M} is equal to (M_1, M_2, \dots, M_n) and the elements of matrix \mathbf{k} are linear combinations of the coefficients k_{ij} . The solution to equation (12) describes the adjustment of all reservoirs to a steady-state by a finite sum of exponential decay functions (Lasaga, 1980). The time-scales of the exponential decay factors correspond to the non-zero eigenvalues of the matrix \mathbf{k} . The response time of the system, τ_{cycle} , may be defined by:

$$\tau_{\text{cycle}} = \frac{1}{|E_1|} \quad (13)$$

where E_1 is the non-zero eigenvalue with smallest absolute value (Lasaga, 1980). The treatment can be generalized by adding an external forcing function on the right-hand side of equations (11) and (12).

As an illustration of the concept introduced above, let us consider a coupled two-reservoir system with no external forcing (Fig. 4-5). The dynamic behavior of this system is governed by the two differential equations:

$$\begin{aligned} \frac{dM_1}{dt} &= -k_{12}M_1 + k_{21}M_2 \\ \frac{dM_2}{dt} &= k_{12}M_1 - k_{21}M_2 \end{aligned} \quad (14)$$

the expression of conservation of mass

$$M_1 + M_2 = M_T \quad (15)$$

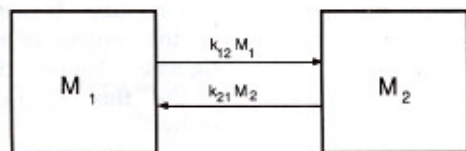


Fig. 4-5 A coupled two-reservoir system with fluxes proportional to the content of the emitting reservoirs.

and the initial condition

$$\begin{aligned} M_1(t=0) &= M_1^0 \\ M_2(t=0) &= M_2^0 = M_T - M_1^0 \end{aligned} \quad (16)$$

Equations (14) can be written in matrix form as:

$$\frac{d\mathbf{M}}{dt} = \mathbf{k}\mathbf{M} \quad (17)$$

where \mathbf{M} is the vector (M_1, M_2) describing the contents of the two reservoirs and \mathbf{k} the matrix:

$$\begin{pmatrix} -k_{12} & k_{21} \\ k_{12} & -k_{21} \end{pmatrix}$$

The eigenvalues of \mathbf{k} are the solutions to the equation

$$\begin{vmatrix} -k_{12} - \lambda & k_{21} \\ k_{12} & -k_{21} - \lambda \end{vmatrix} = (-k_{12} - \lambda)(-k_{21} - \lambda) - k_{12}k_{21} = 0 \quad (18)$$

$\lambda_1 = 0$ and $\lambda_2 = -(k_{12} + k_{21})$. The general solution to equation (17) can be written as:

$$\mathbf{M}(t) = \psi_1 \exp(\lambda_1 t) + \psi_2 \exp(\lambda_2 t) \quad (19)$$

where ψ_1 and ψ_2 are the eigenvectors of the matrix \mathbf{k} . In our case, we have:

$$\mathbf{M}(t) = \psi_1 + \psi_2 \exp(-(k_{12} + k_{21})t) \quad (20)$$

or, in component form and in terms of the initial conditions:

$$\begin{aligned} M_1(t) &= \frac{k_{21}}{k_{12} + k_{21}} M_T + \left(M_{10} - \frac{k_{21} M_T}{k_{12} + k_{21}} \right) \\ &\quad \times \exp[-(k_{12} + k_{21})t] \\ M_2(t) &= \frac{k_{12}}{k_{12} + k_{21}} M_T + \left(M_{20} - \frac{k_{12} M_T}{k_{12} + k_{21}} \right) \\ &\quad \times \exp[-(k_{12} + k_{21})t] \end{aligned} \quad (21)$$

It is seen that in the steady-state the total mass is distributed between the two reservoirs in proportion to the sink coefficients (in reverse proportion to the turnover times), independent of the initial distribution.

In this simple case, there is only one time-scale characterizing the adjustment process, that is $(k_{12} + k_{21})^{-1}$. This is also the response time, τ_{cycle} , as defined by equation (13):

$$\tau_{\text{cycle}} = \frac{1}{k_{12} + k_{21}} \quad (22)$$

or if expressed in terms of the turnover times of the two reservoirs:

$$\tau_{\text{cycle}}^{-1} = \tau_{01}^{-1} + \tau_{02}^{-1} \quad (23)$$

The response time in this simple model will depend on the turnover times of both reservoirs and will always be shorter than the shortest of the two turnover times. If τ_{01} is equal to τ_{02} , τ_{cycle} will be equal to half of this value.

An investigation of the dynamic behavior of a coupled three-reservoir system using the techniques described above is included in the list of problems at the end of the chapter.

It may be noted that the steady-state solution of equation (12) is not necessarily unique. This can easily be seen in the case of the four-reservoir system shown in Fig. 4-6. In the steady-state, all material will end up in the two accumulating reservoirs at the bottom. However, the distribution between these two reservoirs will depend on the amount initially located in the two upper reservoirs.

Before turning to non-linear situations, let us consider two specific examples of coupled linear systems. The first describes the dynamic behavior of a multi-reservoir system, the second represents a steady-state situation of an open two-reservoir system.

Example 1

As a specific example of a time-dependent linear

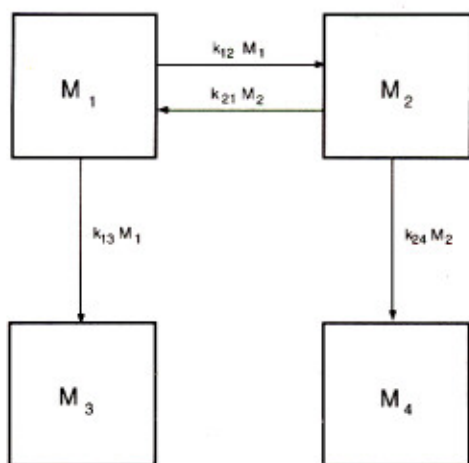


Fig. 4-6 Example of a coupled reservoir system where the steady-state distribution of mass is not uniquely determined by the parameters describing the fluxes within the system but also by the initial conditions (see text).

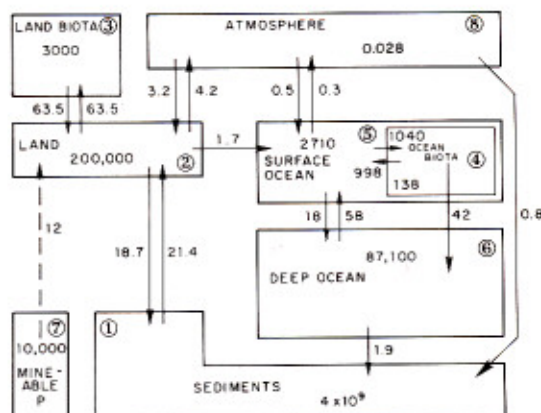


Fig. 4-7 The phosphorus cycle: Phosphorus contents are in units of Tg P, and transfer rates are in units of Tg P/year. Adapted from Lerman *et al.* (1975) with the permission of the Geological Society of America.

system, we may take the model of the phosphorus cycle as formulated by Lerman *et al.* (1975; cf. Fig. 4-7). These authors used a computer to solve the system of equation (11) with a time-dependent source term added to represent the transient situation with an exponentially increasing industrial mining input (7% increase per year). The same situation was studied in a more elegant way by Lasaga (1980) with the aid of matrix algebra. The evolution of the phosphorus content of the various reservoirs (except the sediments) during the first 70 years is shown in Table 4-1. Within this time-frame, the only noticeable change is seen to occur in the land reservoir. Lasaga showed that the adjustment time-scale of the system, τ_{cycle} , is 53 000 years. This is much shorter than the turnover time of the sediment reservoir (2×10^8 years) but much longer than the turnover times of all other reservoirs. This cycle is described in greater detail in Chapter 14.

Example 2

As a much simpler example, let us consider a system consisting of two connected reservoirs (Fig. 4-8). Steady-state is assumed to prevail. Material is introduced at a constant rate Q in reservoir 1. Some of this material is removed (S_1) and the rest (T) is transferred to reservoir 2, from which it is removed at a rate S_2 . The turnover times (average residence times) of the two reservoirs and of the combined reservoir (defined as the sum of the two reservoirs)

Table 4-1 Response of phosphorus cycle to mining output

Time	Land	Land biota	Oceanic biota	Surface ocean	Deep ocean
0 years	200 000	3000	138	2710	87 100
10 years	200 173	3000	138	2710	87 100
20 years	200 522	3001	138	2710	87 100
30 years	201 224	3003	138	2710	87 100
40 years	202 636	3008	138	2710	87 100
50 years	205 481	3018	138	2710	87 100
60 years	211 208	3018	138	2711	87 100
70 years	222 741	3078	138	2712	87 101

Notes: Phosphorus amounts are given in Tg P (1 Tg = 10^{12} g). Initial contents and fluxes as in Fig. 4-7 (system at steady-state). In addition, a perturbation is introduced by the flux from reservoir 7 (mineable phosphorus) to reservoir 2 (land phosphorus), which is given by $12 \exp(0.07t)$ in units of Tg P/year.

are easily calculated to be:

$$\tau_{01} = \frac{M_1}{T + S_1} = \frac{M_1}{Q} \quad (24)$$

$$\tau_{02} = \frac{M_2}{S_2} = \frac{M_2}{T} \quad (25)$$

$$\begin{aligned} \tau_0 &= \frac{M_1 + M_2}{S_1 + S_2} = \frac{M_1 + M_2}{Q} = \frac{M_1}{Q} + \frac{M_2}{S_2} \cdot \frac{S_2}{Q} \\ &= \frac{M_1}{Q} + \frac{M_2}{S_2} \cdot \frac{T}{Q} = \tau_{01} + \alpha \tau_{02} \end{aligned} \quad (26)$$

where $\alpha = T/Q$ is the fraction of the material passing through reservoir 1 that is transferred to reservoir 2.

In the special case where $S_1 = 0$, $T = Q$, and $\alpha = 1$ (all material introduced in reservoir 1 is transferred to reservoir 2), the turnover time of the combined reservoir equals the sum of the turnover times of the individual reservoirs.

Among other situations, this two-reservoir model has been applied to sulfur in the atmosphere with

SO₂-sulfur as one reservoir and sulfate-sulfur as the other (Rodhe, 1978).

4.4.2 Non-linear Systems

In many situations, the assumption about linear relations between removal rates and reservoir contents is invalid and more complex relations have to be assumed. No simple theory exists for treating the various possible non-linear situations. The following discussion will be limited to a few examples of non-linear reservoir/flux relations and cycles. For a more comprehensive discussion, see the review by Lasaga (1980).

Consider a single reservoir with a constant rate of supply and a removal rate proportional to the square of the reservoir content. The equation governing the rate of change of the reservoir content is:

$$\frac{dM}{dt} = Q - BM^2 \quad (27)$$

If $M(0) = 0$, the solution to this equation is:

$$M = \sqrt{\frac{Q}{B}} \cdot \frac{1 - \exp(-2\sqrt{QB}t)}{1 + \exp(-2\sqrt{QB}t)} \quad (28)$$

This is graphically illustrated in Fig. 4-9. Initially, the mass increases almost linearly with time. After the time $1/2\sqrt{(QB)}$, the removal term becomes effective and the mass levels off. M eventually reaches a steady-state equal to $\sqrt{(Q/B)}$, but the response time-scale is not as easily defined as in the linear case. Relative to a simple exponential relaxation process,

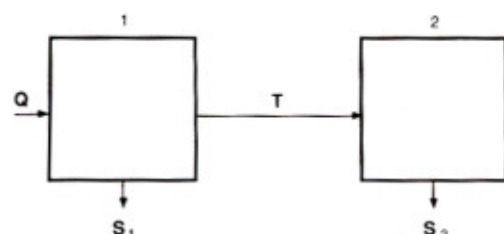


Fig. 4-8 An open two-reservoir system.

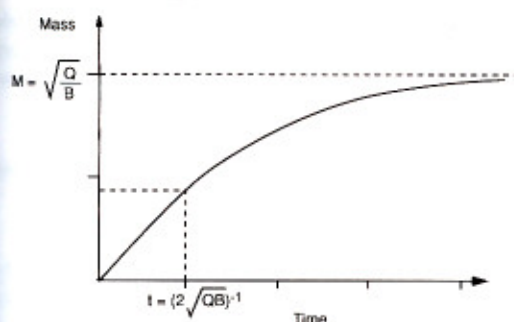


Fig. 4-9 The shape of the function given in equation (28).

the adjustment given by equation (28) is more rapid initially, and slower as time progresses.

In general, if the removal flux is dependent upon the reservoir content raised to the power α ($\alpha \neq 1$), i.e. $S = BM^\alpha$, the adjustment process will be faster or slower than the steady-state turnover time depending on whether α is larger or smaller than 1 (Rodhe and Björkström, 1979).

A similar simple non-linear adjustment process is described by the equation:

$$\frac{dM}{dt} = AM - BM^2 \quad (29)$$

which is a common model for the growth of biological systems (it is called logistical growth). The term AM represents exponential growth (unlimited supply of space and nutrients) and the term BM^2 is a removal term, a negative feedback effect of "crowdedness". Initially (where $AM_0 \gg BM_0^2$), the growth will first be close to exponential and will then gradually level off to the equilibrium value A/B (Fig. 4-10).

An important example of non-linearity in a bio-

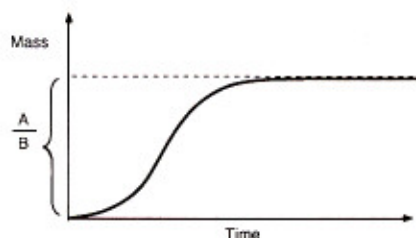


Fig. 4-10 Shape of "logistical growth". The rate of change increases slowly initially. The rate of growth reaches a maximum and eventually drops to zero as the mass levels off, approaching the value A/B .

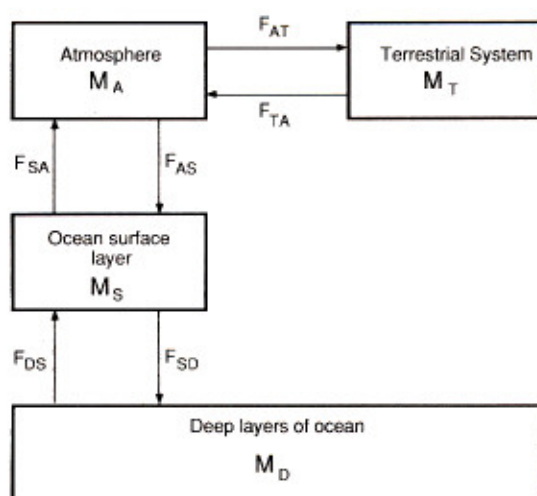


Fig. 4-11 Simplified model of the biogeochemical carbon cycle. Adapted from Rodhe and Björkström (1979) with the permission of the Swedish Geophysical Society.

geochemical cycle is the exchange of carbon dioxide between the ocean surface water and the atmosphere and between the atmosphere and the terrestrial system. To illustrate some effects of these non-linearities, let us consider the simplified model of the carbon cycle shown in Fig. 4-11. M_s represents the sum of all forms of dissolved carbon (CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-}). The ocean to atmosphere flux is related to the dissolved species $\text{CO}_2(\text{aq})$, and this flux is related to the total carbon content in the surface layer (M_s) by:

$$F_{SA} = k_{SA} M_s^{\alpha_{SA}} \quad (30)$$

where the exponent α_{SA} (the buffer factor) is about 9. The buffer factor results from the equilibrium between $\text{CO}_2(\text{aq})$ and the more prevalent forms of dissolved carbon. This effect is discussed further in Chapter 11. As a consequence of this strong dependence of F_{SA} on M_s , a substantial increase in CO_2 in the atmosphere is balanced by a small increase of M_s .

Similarly, the flux from the atmosphere to the terrestrial system may be represented by the expression:

$$F_{AT} = k_{AT} M_A^{\alpha_{AT}} \quad (31)$$

The exponent α_{AT} is considerably less than unity owing to the fact that CO_2 generally is not the limiting factor for vegetation growth. This means

Table 4-2 Steady-state carbon contents (unit: Pg = 10^{15} g) for the four-reservoir model of Fig. 4-11 during the unperturbed (pre-industrial) situation, after the introduction of 1000 Pg carbon, and after the introduction of 6000 Pg carbon

	Pre-industrial content (Pg)	After 1000 Pg		After 6000 Pg	
		Content (Pg)	% increase	Content (Pg)	% increase
Atmosphere	700	840	20	1880	170
Terrestrial system	3 000	3 110	4	3 655	22
Ocean surface layer	1 000	1 020	2	1 115	12
Deep ocean	35 000	35 730	2	39 050	12

that even a substantial increase in M_A does not produce a corresponding increase in F_{AT} .

4.5 Coupled Cycles

Assuming that the carbon cycle of Fig. 4-11 will remain a closed system over several thousands of years, we may ask the question of how the equilibrium distribution within the system would change after the introduction of a certain amount of fossil carbon. Table 4-2 contains the answer for two different assumptions about the total input. The first (1000 Pg) corresponds to the total input from fossil fuel up to about the year 2000; the second (6000 Pg) is roughly equal to the now known accessible reserves of fossil carbon (Keeling and Bacastow, 1977).

An important class of cycles with non-linear behavior is represented by situations when coupling occurs between cycles of different elements. The behavior of coupled systems of this type has been studied in detail by, for example, Prigogine (1967). In these systems, multiple equilibria are sometimes possible and oscillatory behavior can occur. There have been recent suggestions that atmospheric systems of chemical species, coupled by chemical reactions, could exhibit multiple equilibria under realistic ranges of concentration (Fox *et al.*, 1982; White, 1984). However, no such situations have been confirmed by measurements.

If all fluxes are proportional to the reservoir contents, the percentage change in reservoir content will be equal for all the reservoirs. The non-linear relations discussed above give rise to substantial variations between the reservoirs. Note that the atmospheric reservoir is much more significantly perturbed than any of the other three reservoirs. Even in the case with a 6000-Pg input, the carbon content of the oceans does not increase by more than 12% in the steady-state.

4.6 Note on Transport Processes

On the other hand, with "only" 1000 Pg emitted into the system, i.e. less than 3% of the total amount of carbon in the four reservoirs, the atmospheric reservoir would still remain significantly affected (20%) in the steady-state. In this case, the change in oceanic carbon would be only 2% and hardly noticeable. The steady-state distributions are independent of where the addition occurs. If the CO_2 from fossil fuel combustion were collected and dumped into the ocean, the final distribution would still be the same.

In this chapter to date, little consideration has been given to the nature of the transport processes responsible for fluxes of material between and within reservoirs. This appendix includes a very brief discussion of some of the processes that are important in the context of global biogeochemical cycles. More comprehensive treatments can be found in textbooks on geology, oceanography, and meteorology, and in reviews such as Lerman (1979) and Liss and Slinn (1983).

4.6.1 Advection, Turbulent Flux, and Molecular Diffusion

If all fluxes were proportional to the reservoir content, i.e. if the buffer factor had been unity, all reservoirs would be equally affected: 15% in the 6000-Pg case and 2.5% in the 1000-Pg case.

Let us consider a fluid in which a tracer i is mixed. A flux of the tracer within the fluid can be brought

about either by organized fluid motion or by molecular diffusion. These two flux processes can be written as:

$$F_{i1} = Vq_i \rho = Vc_i \quad (32)$$

and

$$F_{i2} = -D_i \rho \nabla q_i \quad (33)$$

where F_{i1} and F_{i2} denote the flux vectors of the tracer (dimensions: mass/length² time), V the fluid velocity vector (length/time), ρ the density of the fluid (mass/length³), q_i the tracer mixing ratio (mass/mass), c_i the mass concentration of the tracer (mass/length³), D the molecular diffusivity (length²/time), and ∇ the gradient operator (as length⁻¹). The expression ∇q_i denotes the vector ($\partial q_i/\partial x, \partial q_i/\partial y, \partial q_i/\partial z$).

The continuity of tracer mass is expressed by the equation

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= -\nabla \cdot F_i + Q - S = -\nabla \cdot (F_{i1} + F_{i2}) + Q - S \\ &= -\nabla \cdot (Vc_i) + \nabla \cdot (D_i \rho \nabla q_i) + Q - S \end{aligned} \quad (34)$$

where Q and S represent production and removal of the tracer (mass/length³ time). Here $\nabla \cdot F_i$ denotes the scalar quantity:

$$\frac{\partial F_{ix}}{\partial x} + \frac{\partial F_{iy}}{\partial y} + \frac{\partial F_{iz}}{\partial z}$$

If variations in fluid density and diffusivity can be neglected, we have:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot (Vc_i) + D\nabla^2 c_i + Q - S \quad (35)$$

In most situations, a fluid would be turbulent, implying that the velocity vector, as well as the concentration c_i , exhibits considerable variability on time-scales smaller than those of prime interest. This situation can be described by writing these quantities as the sum of an average quantity (normally a time average) and a perturbation:

$$\begin{aligned} V &= \bar{V} + V' \\ c_i &= \bar{c}_i + c'_i \end{aligned}$$

From equation (32), the transport flux F_{i1} then becomes:

$$\begin{aligned} F_{i1} &= (\bar{V} + V')(\bar{c}_i + c'_i) \\ &= \bar{V}\bar{c}_i + \bar{V}c'_i + V'\bar{c}_i + V'c'_i \end{aligned} \quad (36)$$

and its average value

$$\bar{F}_{i1} = \bar{V}\bar{c}_i + \overline{V'c'} \quad (37)$$

Note that the averages of V' and c' are equal to zero. The continuity equation can now be written as:

$$\frac{\partial \bar{c}_i}{\partial t} = -\nabla \cdot (\bar{V}\bar{c}_i) - \nabla \cdot (\overline{V'c'}) + D\nabla^2 \bar{c}_i + Q - S \quad (38)$$

The two terms on the right-hand side of equation (37) describe transport by *advection* and by *turbulent flux*, respectively. The separation of the motion flux into advection and turbulent flux is somewhat arbitrary; depending upon the circumstances, the averaging time can be anything from a few minutes to a year or even more.

Because in most situations the perturbation quantities (V' and c'_i) are not explicitly resolved, it is not possible to evaluate the turbulent flux term directly. Instead, it has to be related to the distribution of averaged quantities – a process referred to as parameterization. A common assumption is to relate the turbulent flux vector to the gradient of the averaged tracer distribution [in analogy with the molecular diffusion expression in equation (33)]:

$$(F_{i2})_{\text{turb}} = V'c'_i = -k_{\text{turb}} \nabla \bar{c}_i \quad (39)$$

The coefficient k_i thus introduced (dimension: length²/time) is called the turbulent, or eddy, diffusivity. In the general case, the eddy diffusivity is given separate values for the three spatial dimensions.

It must be remembered that the eddy diffusivities are not constants in any real sense (like the molecular diffusivities) and that their numerical values are very uncertain. The assumption underlying equation (39) is therefore open to question.

In most cases, the term expressing the divergence of the molecular flux in equation (38) ($D\nabla^2 \bar{c}_i$) can be neglected compared to the other two transport terms. Important exceptions occur, e.g. in a thin layer of the atmosphere close to the surface and in similar layers of the oceans close to the bottom and to the surface (viscous sublayers). Molecular diffusion is also an important transport process in the upper atmosphere, at heights above 100 km.

Order of magnitude values for vertical eddy diffusivity in the atmosphere and the ocean are shown in Fig. 4-12. The values for the viscous layers represent molecular diffusivities of a typical air molecule like N_2 .

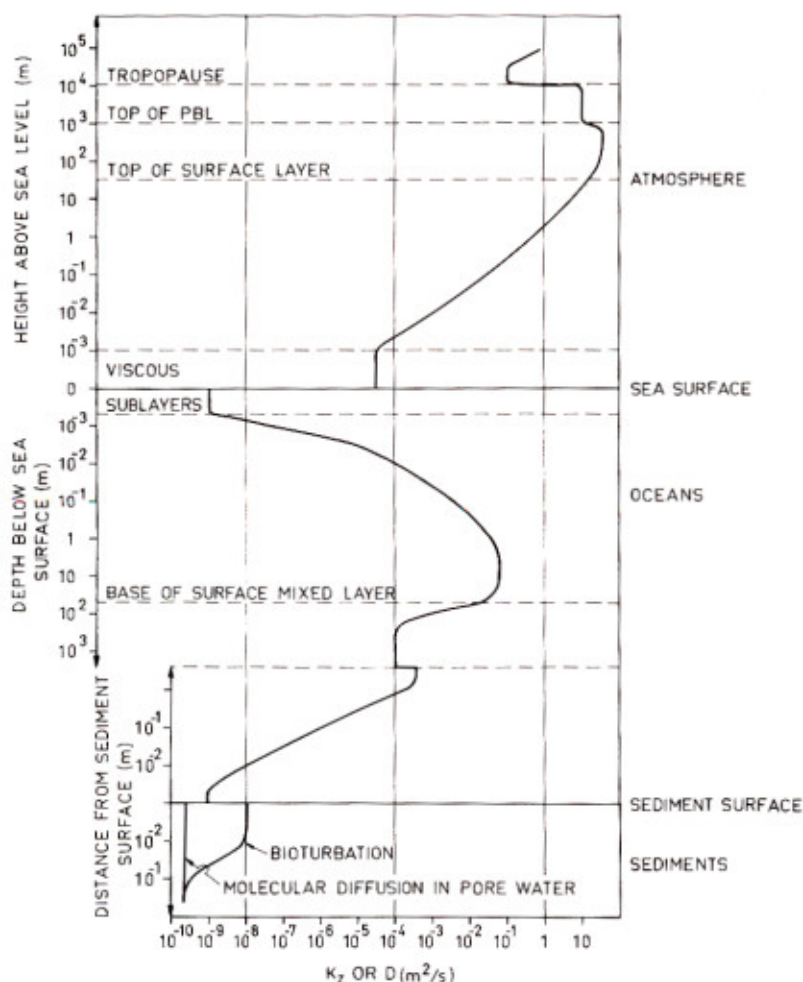


Fig. 4-12 Orders of magnitude of the average vertical molecular or turbulent diffusivity (whichever is largest) through the atmosphere, oceans, and uppermost layer of ocean sediments.

4.6.2 Other Transport Processes

Under some circumstances, transport processes other than fluid motion and molecular diffusion can be important. One important example is *sedimentation* due to gravity acting on particulate matter submerged in a fluid, e.g. removal of dissolved sulfur from the atmosphere by precipitation scavenging, transport of organic carbon from the surface waters to the deep layers and to the sediment by settling detritus. The rate of transport by sedimentation is determined essentially by the size and density of the particles and by the drag exerted by the fluid.

Geochemically significant mixing and transport can sometimes be accomplished by biological processes. An interesting example is redistribution of sediment material caused by the movements of worms and other organisms (*bioturbation*). Exchange processes between the atmosphere and oceans and between the oceans and the sediments are treated below in separate sections.

4.6.3 Air-Sea Exchange

4.6.3.1 Gas transfer

The magnitude and direction of the net flux, F , of any gaseous species across an air-water interface,

counted positive if the flux is directed from the atmosphere to the ocean, is related to the difference in concentration, Δc , in the two phases by the relation:

$$F = K\Delta c \quad (40)$$

Here $\Delta c = c_a - K_H c_w$ with c_a and c_w representing the concentrations in the air and water respectively and K_H the Henry's Law constant. The parameter K , linking the flux and the concentration difference, has the dimension of a velocity. It is often referred to as the transfer (or piston) velocity. The reciprocal of the transfer velocity corresponds to a resistance to transfer across the surface. The total resistance ($R = K^{-1}$) can be viewed as the sum of an air resistance (R_a) and a water resistance (R_w):

$$R = R_a + R_w = \frac{1}{k_a} + \frac{K_H}{\alpha k_1} \quad (41)$$

The parameters k_a and k_1 are the transfer velocities for chemically unreactive gases through the viscous sublayers in the air and water, respectively. They relate the flux F to the concentration gradients across the viscous sublayers through expressions similar to equation (40):

$$\begin{aligned} F &= k_a(c_a - c_{a,i}) \\ F &= k_1(c_{w,i} - c_w) \end{aligned} \quad (42)$$

Here $c_{a,i}$ and $c_{w,i}$ are the concentrations right at the interface (cf. Fig. 4-13). They are related by $c_{a,i} = K_H c_{w,i}$.

The parameter α in equation (41) quantifies any enhancement in the value of k_1 due to chemical reactivity of the gas in the water. Its value is unity for an unreactive gas; for gases with rapid aqueous phase reactions (e.g. SO_2), much higher values can occur.

A comparison of the resistance in air and water for different gases shows that the resistance in the water dominates for gases with low solubility that are unreactive in the aqueous phase (e.g. O_2 , N_2 , CO_2 , CH_4). For gases of high solubility or rapid aqueous chemistry (e.g. H_2O , SO_2 , NH_3), processes in the air control the interfacial transfer.

The numerical values of the transfer velocity K for the different gases are not well established. Its magnitude depends on such factors as wind speed, surface waves, bubbles, and heat transfer. A globally averaged value of K often used for CO_2 is about 10 cm/h. Transport at the sea-air interface is also discussed in Chapter 9 (for a review, see Liss, 1983).

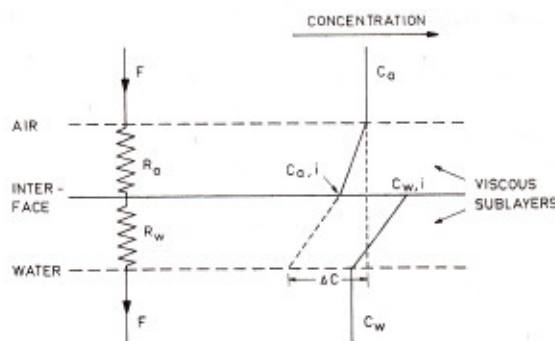


Fig. 4-13 A simplified model of flux resistances and concentration gradients in the viscous sublayers at the air-sea interface.

4.6.3.2 Transfer of particles

Liquid water, including its soluble and insoluble constituents, is transferred from the oceans to the atmosphere when air bubbles in the water rise to the surface. These bubbles form from air trapped by breaking waves called "whitecaps". As the bubbles burst at the surface, water droplets are injected into the atmosphere. These water droplets are small enough to remain airborne for several hours. Whitecaps begin to form in winds common over the oceans, and significant quantities of sea salt made airborne in this way are transported to the continents and deposited in coastal areas.

The flux of particles in the other direction, deposition on the ocean surface, occurs intermittently in precipitation (*wet* deposition) and more continuously as a direct uptake by the surface (*dry* deposition). These fluxes may be represented by a product of the concentration of particulate matter in air close to the surface and parameters often referred to as deposition velocities:

$$F = F_w + F_d = (v_w + v_d) c_a$$

The deposition velocities depend on the size distribution of the particulate matter, on the frequency of occurrence and intensity of precipitation, the chemical composition of the particles, the wind speed, nature of the surface, etc. Typical values of v_w and v_d for particles below about 1 μm in diameter are in the range 0.1–1.0 cm/s (Slinn, 1983). The average residence time in the atmosphere for such particles is of the order of a few days.

4.6.4 Sediment-Water Exchange

The sediment surface separates a mixture of solid sediment and interstitial water from the overlying water. Growth of the sediment results from accumulation of solid particles and inclusion of water in the pore space between the particles. The rates of sediment deposition vary from a few millimeters per 1000 years in the pelagic ocean up to centimeters per year in lakes and coastal areas. The resulting flux of solid particles to sediment surface is normally in the range $0.006\text{--}6.0\text{ kg/m}^2\text{ year}$ (Lerman, 1979). The corresponding flux of materials dissolved in the trapped water is $10^{-6}\text{--}10^{-3}\text{ kg/m}^2\text{ year}$. Chemical species can also be transported across the sediment surface by other transport processes. The main processes are (Lerman, 1979):

1. Sedimentation of solids (mineral, skeletal, and organic materials).
2. Flux of dissolved material and water into sediment, owing to the growth of the sediment column.
3. Upward flow of pore water and dissolved material caused by pressure gradients.
4. Molecular diffusional fluxes in pore water.
5. Mixing of sediment and water at the interface (bioturbation and water turbulence).

An estimate of the advective fluxes (processes 1, 2, and 3) requires knowledge of the concentration of the species in solution and in the solid particles as well as of the rates of sedimentation and pore water flow. The diffusive type processes 4 and 5 depend on vertical gradients of the concentrations of the species as well as on the diffusivities. In regions where bioturbation occurs, the effective diffusivity in the uppermost centimeters of the sediments can be more than that due to molecular diffusion in the pore water alone (cf. Fig. 4-12).

4.7 Note on Times of Mixing in the Atmosphere and Oceans

It is often important to know how long an element spends in one environment before it is transported somewhere else. For example, if a time-scale characterizing a chemical or physical transformation process in a region has been estimated, a comparison with the time-scale characterizing the transport away from this region will tell which process is likely to dominate.

The question of residence time and its definition in a steady-state reservoir was discussed earlier in this chapter. In such cases, the average residence time in the reservoir was shown to be equal to the turnover time $\tau_0 = M/S$, where M is the mass of the reservoir and S the total flux out of it. It is important to note that if one considers the exchange between two reservoirs of different mass, the time-scale of exchange will be different depending upon whether the perspective is from the small or the big reservoir. An interesting example is that of mixing between the troposphere and stratosphere in the atmosphere. Studies of radioactive nuclides injected into the lower stratosphere by bomb testing have shown that the time-scale characterizing the exchange between the lower stratosphere and troposphere is one to a few years. This means that a "particle" injected in the lower stratosphere will stay for this time, on average, before entering the troposphere. On the other hand, a gas molecule like N_2O , which is chemically stable in the troposphere, will spend several decades in the troposphere before it is mixed up into the lower stratosphere, where it is decomposed by photochemical processes. Thus, even though the gross flux of air from the troposphere to the stratosphere, F , is equal to the gross flux of air from the stratosphere to the troposphere, the time-scale of mixing between these two reservoirs is several decades from the tropospheric point of view, τ_T , but only a few years as seen from the stratosphere, τ_S . The reason for the difference is, of course, the small mass of the stratosphere, M_S , as compared to the troposphere, M_T . Formally, we can write:

$$\frac{\tau_S}{\tau_T} = \frac{M_S/F}{M_T/F} = \frac{M_S}{M_T} \approx 0.1$$

Time-scales of transport can also be applied to situations when no well-defined reservoirs can be defined. If the dominant transport process is advection by mean flow or sedimentation by gravity, the time-scale characterizing the transport between two places is simply $\tau_{\text{adv}} = L/V$, where L is the distance and V the transport velocity. Given a typical wind speed of 20 m/s in the mid-latitude tropospheric westerlies, the time of transport round the globe would be about 2 weeks.

In situations where the transport is governed by diffusive processes, a time-scale of transport can be defined as:

$$\tau_{\text{turb}} = \frac{L^2}{D}$$

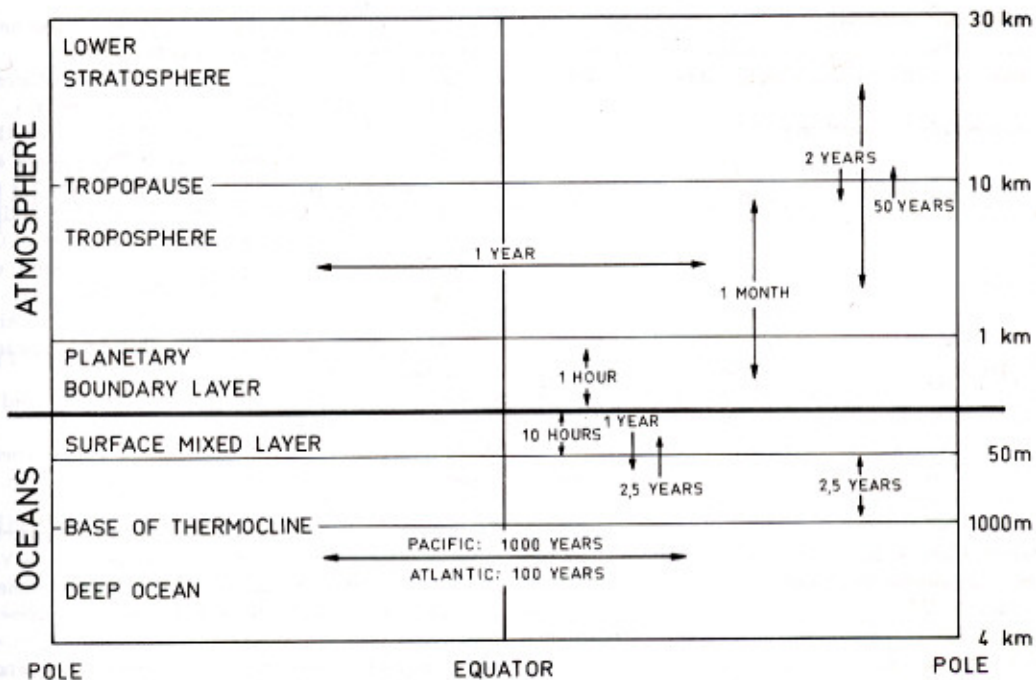


Fig. 4-14 Rough estimates of characteristic time for exchange of air and water respectively, between different parts of the atmosphere and oceans. All heights and depths are variable.

where L is the distance and D the diffusivity (molecular or turbulent). Applying this definition to the vertical mixing through the surface mixed layer of the ocean, assuming the depth of the layer to be 50 m and the turbulent diffusivity $0.1 \text{ m}^2/\text{s}$ we get:

$$\tau_{\text{turb}} = \frac{(50)^2}{0.1} \text{ s} \approx 7 \text{ h}$$

Some important time-scales characterizing the transport within the oceanic and atmospheric environments are summarized in Fig. 4-14. In view of the somewhat ambiguous nature of the definitions of these time scales, the numbers should not be considered as more than indications of the magnitudes.

Acknowledgement. I wish to thank Anders Björkström for valuable comments on the manuscript.

Questions

4-1 Consider a reservoir with two separate sources Q_1 and Q_2 and a single sink S . The magnitudes of Q_1 and S

and their uncertainties have been estimated to be 75 ± 20 and 100 ± 30 (arbitrary units). Assuming that there is no direct way of estimating Q_2 , how would you derive its magnitude and uncertainty range from budget considerations? What assumption must be made regarding the reservoir?

4-2 Calculate the turnover time of carbon in the various reservoirs given in Fig. 4-2.

4-3 What is the relation between the turnover time τ_0 , the average transit time τ_r , and the average age τ_a in a reservoir where all "particles" spend an equal time in the reservoir?

4-4 Consider a reservoir with a source flux Q and two sink fluxes S_1 and S_2 . S_1 and S_2 are proportional to the reservoir content M with proportionality constants k_1 and k_2 . The values of k_1 and k_2 are $(1/\text{year})$ and $(0.2/\text{year})$, respectively. The system is initially in steady-state with $M = M_0$ and $Q = S_{01} + S_{02}$. Describe the change in time of M if the source is suddenly reduced to half its initial value. What is the response time of the reservoir?

4-5 Consider the water balance of a lake with a constant source flux Q . This outlet is of the "threshold" type where the sink is proportional to the mass of water above a threshold value M_1 ; $S = k(M - M_1)$. Calculate the turnover time of water at steady-state and the response time relative to changes in Q .

- 4-6 For the more mathematically inclined, investigate the dynamic behavior of a coupled linear three-reservoir model using the technique outlined in Section 4.4.

Answers can be found on p. 365.

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