

$$\begin{aligned} & \text{tonnes of sulfur from coal combustion in 1980} \\ &= \frac{90 \times 10^{18} \text{ J}}{29.3 \times 10^9 \text{ J/tonne(coal)}} \times 0.025 \text{ tonnes(S)/tonne(coal)} \quad (3) \\ &= 7.7 \times 10^7 \text{ tonnes(S)}. \end{aligned}$$

A mole of any material has a mass of M grams, where M is the molecular mass of the substance (number of protons and neutrons in a molecule). The following units conversion is used to convert tonnes to moles for any material, A :

$$\text{moles of } A = \frac{\text{tonnes}(A) \times [10^6 \text{ g}(A)/\text{tonne}(A)]}{M[\text{g}(A)/\text{mole}(A)]} \quad (4)$$

Using the fact that the atomic (and molecular) mass¹¹ of S is 32, and substituting the actual numbers into Eq. 4, we get:

$$\begin{aligned} & \text{moles(S) from coal combustion in 1980} \\ &= \frac{[7.7 \times 10^7 \text{ tonnes(S)}] \times [10^6 \text{ g(S)/tonne(S)}]}{32 \text{ g(S)/mole(S)}} \quad (5) \\ &= 2.4 \times 10^{12} \text{ moles(S)}. \end{aligned}$$

EXERCISE 1: Using additional data from the Appendix (VII.3), calculate the number of tonnes of cadmium, lead, zinc, selenium, mercury, and arsenic contained in the coal combusted worldwide 1980. Compare the rates at which these substances are emitted into the atmosphere worldwide from coal combustion with the natural background rates of mobilization to the atmosphere given in the Appendix (IX), under the assumption that all the trace substances found in fossil fuel are emitted into the atmosphere when the fuel is burned. In practice, some portion of the trace substances in fuels is left behind as solid waste in the form of ash when the fuel is burned. The pathways that the substances in fuel follow (through air, water, soil, and living organisms) and the chemical transformations they undergo in the environment (including reactions that can render them more or less toxic than they were in their initial emitted form) depend on many factors. Specific examples will be described later in this book.

EXERCISE 2: For further practice at converting units, use the data in the Appendix on the energy content of specified quantities of fossil fuels to calculate the present world's resources of petroleum, coal, and natural gas in units of barrels, metric tons, and cubic meters, respectively.

11. For a substance like molecular oxygen (O_2) consisting of two identical atoms, the molecular mass is twice the atomic mass; but for S or any other molecule consisting of a single atom, the molecular mass equals the atomic mass.

Chapter II

Tools of the Trade

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... having a good question, a fundamental question, and having some tools of inquiry that allow you to take the first step toward an answer—those are the conditions that make for exciting science.

—Herbert A. Simon

Here you will be handed some of the tools that form the core of environmental science. They include residence-time methods and box models, practical methods in thermodynamics and chemical equilibrium kinetics, and a few relatively simple differential equations. (If you are typical, you were probably paralyzed with fear when you read the previous sentence. Relax—we will take it slowly.)

From: "Consider a Spherical Cow" by

John Harte

University Science Books. 1998.

A.

Steady-State Box Models and Residence Times

When the flow of a substance into a lake, the atmosphere, an animal, or any other "box" is equal to the outflow of that substance, then the amount, or "stock," of that substance in the box will be constant. This is called a "steady state" or "equilibrium." The ratio of the *stock* in the box to the *flow rate* (in or out) is called the *residence time*. Thus, if F_{in} is the rate of inflow to the box and F_{out} is the rate of outflow, the steady-state condition is $F_{in} = F_{out}$. Letting M be the stock and T be the residence time, $MF_{in} = MF_{out} = T$. The first problem provides a very simple illustration of the concept of residence time, while the subsequent problems provide practice in applying it. Problems 2 through 5 in this chapter are "one-box" problems, with only a single inflow and a single outflow to worry about in each. Problem 6 is also a "one-box" problem with single inflow and outflow, but the discussion following the solution describes how to deal with multiple flows. In Problem II.7, two boxes are interconnected by flows. Problems II.8 and II.9 also involve connected boxes and treat the case in which a flow or stock is perturbed. The last two problems illustrate the widespread applicability and power of box models. Problem II.10 shows how flow-stock considerations allow estimation of the deposition velocity of airborne particulates, and Problem II.11 shows how a steady-state indoor air concentration of a radioactive isotope can be derived. Later problems in Chapter III illustrate how thinking in terms of flows, stocks, and residence times can help simplify situations more complicated than those treated here.

1. School as a Steady-State System

A college has a constant undergraduate enrollment of 14,000 students. No students flunk out or transfer in from other colleges and so the residence time of each student is four years. How many students graduate each year?

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The residence time of a student is four years, the stock of students is 14,000, and the outflow rate is the graduation rate. It follows from the preceding discussion of steady-state systems that the flow rate in or out of the college is the stock divided by the residence time, or

$$F_{in} = F_{out} = M/T. \quad (1)$$

For our specific problem, this formula becomes:

$$\begin{aligned} \text{graduation rate} &= \frac{\text{total stock of students}}{\text{residence time of students}} = \frac{14,000}{4 \text{ yr}} \\ &= 3,500/\text{yr}. \end{aligned} \quad (2)$$

In this problem, all students spend exactly the same amount of time in college—four years. In many other steady-state situations, each unit of the substance (for example, each molecule of pollutant) comprising the stock spends the residence time in the box only in a statistical sense. The average time spent by all the units is the residence time, but the individual times spent by the units may differ widely. Provided the stock is in a steady state, stock = (inflow or outflow rate) \times (residence time). The flow can be of various types. The movement of students through college illustrates a type of flow in which the components of the stock pass through in an orderly manner so that each component has the same residence time. The subsequent box-model problems in this chapter illustrate the far more typical case of *mixed flow*, in which the inflowing units of stock mix thoroughly in a medium and have differing individual residence times.

EXERCISE 1: A population of cows on a farm is in steady state. The birth rate is 7 calves per year and the average residence time for a cow on the farm is 6 years. How large is the herd?

EXERCISE 2: Suppose there are 100 students enrolled in a graduate program year after year, and that each year 20 get degrees and leave, 5 flunk out, and 25 new students enter the program. (a) What is the average residence time of a student in the program? (b) If

all the students that flunk out do so at the end of their first year, what is the average length of time to get a degree (for those students who do get a degree)? (Hint for b: First determine the number of enrolled students, at any specific time, who will eventually get degrees.)

2. The Water Above

What is the residence time of H₂O in Earth's atmosphere?

.....

The sky is often fairly clear after a big rain storm, so as a rough estimate, the average interval between major precipitation events should be the atmospheric residence time of water. Half of that interval might be a better guess, however, because evaporation and transpiration¹ rates are probably fairly steady during the between-storm interval (see Figure II-1). (Can you see why it makes no difference to this argument that precipitation does not fall synchronously all over the world?) This "hand-waving" argument suggests that the residence time should be very roughly a week, an answer that should underestimate the true solution because the sky is not actually free of all moisture after a storm.

An accurate answer can be obtained by appropriate use of data in the Appendix. Assuming the atmospheric H₂O is in steady state, the

flow of H₂O into the atmosphere, F_w , equals the flow out. The outflow, of course, is the global precipitation rate. From the Appendix (VI.2,3) we learn that $F_w = 5.18 \times 10^{14}$ m³/yr, and that the stock of H₂O in the atmosphere, M_w (which is mostly in vapor, not liquid form), is 1.3×10^{13} m³ (liquid equivalent). The residence time, T_w , is then

$$T_w = \frac{M_w}{F_w} = 0.025 \text{ yr} = 9.1 \text{ days.} \quad (1)$$

The residence time of individual water molecules in the atmosphere may range from fractions of an hour to millenia. T_w , calculated above, is the *average* residence time of all the water molecules in the atmosphere.

EXERCISE 1: What is the residence time of water in all of Earth's oceans?

EXERCISE 2: For further practice at converting units, calculate how much annual precipitation must occur on the average throughout the world, in units of inches of water, to account for the value of F_w .

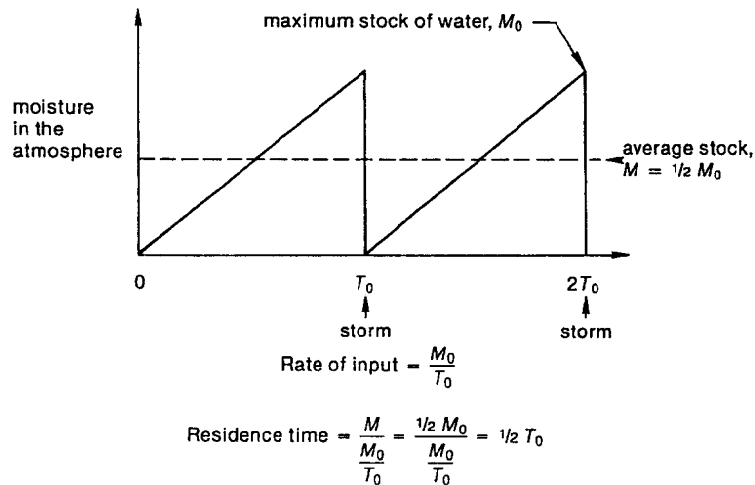


Figure II-1 An hypothesis about the buildup of atmospheric water between storms. This hand-waving argument suggests the residence time of atmospheric water is half the interval between storms.

1. The glossary provides definitions of words like "transpiration" that may be unfamiliar to you. If you come across a word you don't know, check the glossary first.

3. Carbon in the Biosphere

What are the residence times of carbon in continental and marine vegetation?

.....

Take a guess. Trees live for 50 years or more and constitute a large share of continental vegetation. Phytoplankton, accounting for a large share of marine primary productivity, generally come and go in a series of annual blooms and crashes each lasting less than a year. We might therefore expect the residence time of carbon in plants to be on the order of 10–100 years on the land and 0.1–1 year in the oceans.

To be more accurate, we must know the stocks and flows of carbon. The stocks are living biomasses and the flows are net primary productivities. The Appendix provides both of these quantities, in conveniently comparable units—g(C) and g(C)/yr. From this we can obtain

$$\begin{aligned} T_{\text{terrestrial}} &= \frac{\text{stock of living continental biomass}}{\text{continental net primary productivity}} \\ &= \frac{5.6 \times 10^{17} \text{ g(C)}}{5 \times 10^{16} \text{ g(C)/yr}} \\ &= 11.2 \text{ yr} \end{aligned} \quad (1)$$

and

$$\begin{aligned} T_{\text{oceanic}} &= \frac{\text{stock of living marine plants}}{\text{marine net primary productivity}} \\ &= \frac{2 \times 10^{15} \text{ g(C)}}{2.5 \times 10^{16} \text{ g(C)/yr}} \\ &= 0.08 \text{ yr} \approx 1 \text{ month.} \end{aligned} \quad (2)$$

These relations are illustrated in Figure II-2. The considerable uncertainty in the stock and flow data used here (see Appendix) makes these residence times approximate.

Notice that the continental residence time of carbon is considerably shorter than the average lifetime of trees. Even though the woody parts of trees constitute the bulk of living continental biomass, only a part of each tree's annual production adds woody tissue; much of the net primary productivity produces leaves, which have less than a one-year residence time.

Why did we use net primary productivities in this calculation? Had we used data on gross marine and continental primary productivities

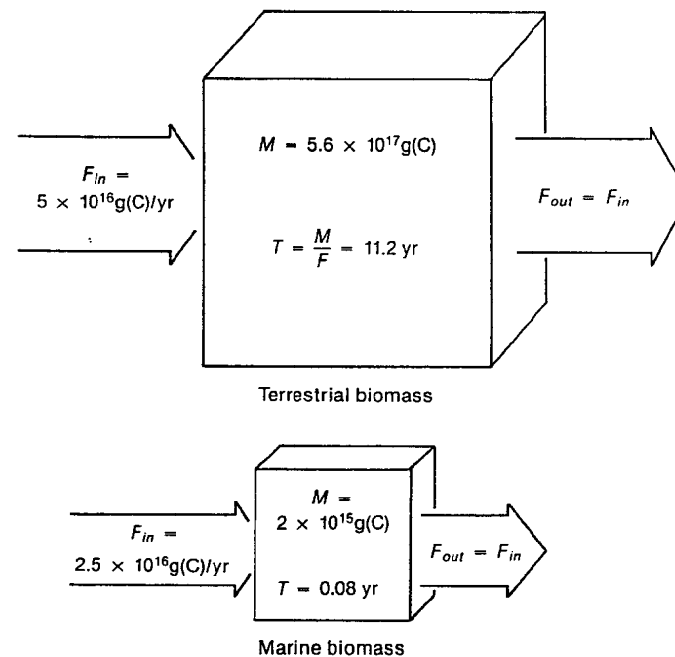


Figure II-2 Stocks and flows of biomass in terrestrial and marine biomasses.

instead, we would have obtained much shorter residence times. Carbon flows relatively quickly through respiratory pathways in organisms. This respiratory flow is not included in net primary productivity. Using net primary productivity yields a residence time that bears a closer relation to the lifetimes of typical organisms (see Exercise 2).

EXERCISE 1: Suppose that the average residence time (ignoring respiratory pathways) of carbon in the phytoplankton in a lake is two weeks. Zooplankton in the lake, grazing upon the phytoplankton, consume 40% of the net primary productivity and have an incorporation efficiency of 25% (i. e., 25% of the phytoplankton biomass they eat is incorporated into zooplankton biomass). In other words, the net productivity of the zooplankton is 0.25×0.40 or 10% of the npp of the algae. If the average residence time (ignoring respiratory pathways) of carbon in zooplankton biomass is six months, estimate the ratio of the average biomass of the zooplankton population to that of the phytoplankton population in the lake. Figure II-3 illustrates the flows in and out of the two stocks of plankton.

* **EXERCISE 2:** In this exercise we explore the relation between residence time of biomass and lifetime of individuals in a steady-state

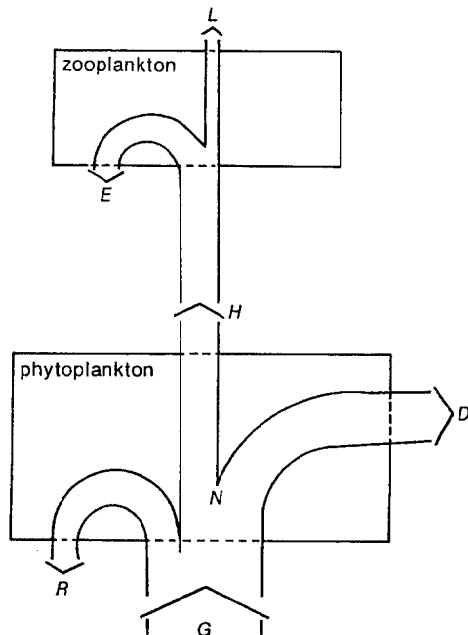


Figure II-3 The flows of carbon in and out of a phytoplankton and zooplankton population in a lake. G is the gross primary productivity of the phytoplankton and R is their respiration rate. $N = G - R$ is net primary productivity. H represents loss of carbon by zooplankton herbivory, and D comprises all other losses. E is excretory and metabolic loss of carbon from the zooplankton population, and $L = H - E$ describes the loss of carbon from the zooplankton population by predation or other forms of death. N and L are the flows used to determine the carbon residence time in the biomass of each population.

population. The residence time, T , of biomass in a population is the interval during which new net production of biomass equals the total average standing crop or stock, M . To relate T to lifetime of individuals, we must know something about the mass-versus-age dependence of the population. Consider two cases: (a) All individuals grow linearly in mass from birth until death. (b) All individuals achieve maximum mass early in life and then maintain a constant mass until death. The first case corresponds very crudely to the situation among plant populations, the second to that among animals. If it is assumed that all individuals in a population die at the same age, A_0 , show that in case a, T equals $A_0/2$ and in case b, T is about equal to A_0 .

* **EXERCISE 3:** Consider a forest in which the residence time for carbon (ignoring respiratory pathways) in the living trees is 15 years,

in leaves is 1 year, and in woody parts (including roots) is 100 years. (a) What is the ratio of leaf biomass to wood biomass, and (b) what fraction of total net productivity does wood productivity constitute?

4. Natural SO₂

Natural sources add sulfur dioxide (SO₂) to the atmosphere at a rate of about 10⁸ tonnes(S)/yr. The background concentration of atmospheric SO₂, measured in remote areas where anthropogenic sources are not likely to have much influence, is about 0.2 parts per billion, by volume [ppb(v)]. What is the residence time of atmospheric SO₂ in the remote regions?

.....

The Appendix notes a total natural background sulfur emission rate of 1.5 × 10¹¹ kg(S)/yr, or equivalently, 1.5 × 10⁸ tonnes(S)/yr. Of this, roughly 10⁸ tonnes(S)/yr comprise hydrogen sulfide (H₂S) and SO₂, while the rest is sulfate (SO₄⁻²). The H₂S is rapidly converted to SO₂ in the atmosphere, whereas the SO₄⁻² is not. Hence we estimate that 10⁸ tonnes(S)/yr of SO₂ is emitted from natural sources.

Because the source term is in units of tonnes(S)/yr, it will be useful to convert the concentration given in the problem, 0.2 ppb(v), into units of tonnes(S). Since the (v) of ppb(v) stands for volume, and ppb stands for parts per billion (one part in 10⁹), every unit volume of atmospheric air contains (on average) 0.2 × 10⁻⁹ unit volumes of SO₂. The use of volumetric comparisons of gases makes sense because of a special property of gases: Every mole (see Problem 1.7) of gas occupies a volume of 22.4 liters at STP.² By comparing gases on a volume-per-volume basis, we are really comparing on a mole-per-mole basis.³

The number of moles of background SO₂ in our atmosphere can now be determined by multiplying the number of moles of air by the molar fraction of SO₂ calculated above (0.2 × 10⁻⁹). So let's determine how many moles of air Earth's atmosphere contains. The mass of our planet's supply of air is 5.14 × 10²¹ g. To calculate the number of moles involved we must divide this by the molecular mass of air. Air, of course, is a mixture of gases. The molar fraction of the mixture that is nitrogen is 78.08%; the molar fraction that is oxygen is 20.95%. Because the molecular masses of N₂ and O₂ are 28 and 32, respectively, the average molecular mass of air is about [(0.7808 × 28) + (0.2095 × 32)]/0.9903 = 28.85. With trace gases included (see Appendix (V.2)), the average molecular mass works out to be 28.96. Dividing 5.14 × 10²¹ g of air by 28.96 g per mole of air yields a planetary total of about 1.8 × 10²⁰ moles of air.

2. Standard temperature (0°C) and pressure (1 atmosphere).

3. A mole of any substance has a mass equal to the molecular mass of the substance and contains 6.02 × 10²³ molecules. The number 6.02 × 10²³ is called Avogadro's number.

The product of moles of air times molar fraction of SO₂ gives (0.2 × 10⁻⁹) × (1.8 × 10²⁰) or 3.6 × 10¹⁰ moles of SO₂. Next, we must calculate the mass of this many moles of SO₂. The molecular mass of S is 32, so a mole of S contains 32 g of S. Therefore, the number of grams of S in atmospheric SO₂ is 32 × 3.6 × 10¹⁰ = 1.15 × 10¹² g(S) = 1.15 × 10⁶ tonnes(S).

We now have a natural background flow of SO₂ to the atmosphere, *F*, given by

$$F = 10^8 \text{ tonnes(S)/yr} \quad (1)$$

and a stock, *M*, given by

$$M = 1.15 \times 10^6 \text{ tonnes(S)}. \quad (2)$$

The residence time, *T*, is equal to *M/F*, or

$$\begin{aligned} T &= \frac{1.15 \times 10^6 \text{ tonnes(S)}}{10^8 \text{ tonnes(S)/yr}} = 0.0115 \text{ yr} \\ &= 4.2 \text{ days}. \end{aligned} \quad (3)$$

EXERCISE 1: Show that an SO₂ atmospheric concentration of 0.2 ppb(v) is equivalent to 0.4 ppb(w), where (w) stands for weight and ppb(w) refers to the number of tonnes (or grams) of SO₂ in 10⁹ tonnes (or grams) of air.

EXERCISE 2: If gases emitted from Earth's surface to the atmosphere are, chemically, relatively nonreactive, and have low solubility in rain, they are likely to remain in the atmosphere for a long time. Under such circumstances, they have a good chance of passing through the tropopause to the stratosphere. A stable, nonreactive gas typically resides in the troposphere for about 10 years before exiting to the stratosphere. In the stratosphere, photochemical reactions may result in a sink, or exit process, for the gas. One such gas is nitrous oxide (N₂O), produced by bacteria in the natural denitrification process. Its chemical inertness gives N₂O safe passage through the troposphere, but in the stratosphere it is photochemically destroyed. The average concentration of N₂O in the troposphere is about 300 ppb(v). What is the global rate of production of N₂O in units of kg(N₂O)/yr?

EXERCISE 3: When gases are emitted to the atmosphere from Earth's surface, diffusion and atmospheric circulation cause the gases to mix. After about three weeks such gases are distributed vertically in the troposphere in such a way that their densities decrease with increasing altitude at the same rate as nitrogen's and oxygen's densities decrease. Qualitatively, how will the ratio of the SO₂ concentration to the N₂ or O₂ concentration depend on altitude within the troposphere?

5. Anthropogenic SO₂

With anthropogenic sources included, what is the globally averaged SO₂ concentration in the atmosphere? What is the SO₂ concentration in industrialized regions like the northeastern United States?

.....

Referring to the Appendix, anthropogenic sulfur emissions to the atmosphere in 1980 were about 8.5×10^7 tonnes(S)/yr.⁴ Therefore, the globally averaged total SO₂ concentration will be about 85% higher than the result derived in Problem II.4, where only natural sources were included in the calculation. Anthropogenic emissions, however, will not be distributed as uniformly in the atmosphere as the background sulfur emissions because the sources are concentrated and the residence time is short compared to the time needed for gases to circle the globe.

Concentrations of atmospheric SO₂ over industrialized regions will vary tremendously, depending on weather conditions. Very importantly, it will also depend on the presence of other substances in the atmosphere that react with SO₂. These substances themselves are often the products of combustion and they can transform SO₂ to some other chemical state—for example, to sulfuric acid, which comprises acid precipitation. The occurrence of these reactions will alter the residence time of SO₂. The residence time approach will not yield a precise answer now, even if the above factors are specified, because the urban air box, or air shed, is not of precise size. Put differently, concentrations of pollutants trail away the further away one is from pollution sources, and the area they flow into and out of has no well-defined boundaries. However, a rough estimate of the concentrations in large industrialized regions like the northeastern United States can be obtained by noting that in four days of residence in the atmosphere, a typical SO₂ molecule will travel in the direction of a prevailing wind of 15 km/hr a distance of $(15 \text{ km/hr}) \times (4 \times 24 \text{ hr}) = 1440 \text{ km}$. Thus, although wind velocity is variable, the northeastern section of the United States (from the latitude of Washington D.C. north, and from the midwest to the Atlantic coast) can be considered an approximate air shed for SO₂ emitted in that region (see Figure II-4).

The Northeast presently emits about 10^7 tonnes(S)/yr, or 12% of the global anthropogenic SO₂, yet it occupies only about 0.2% of Earth's

4. This is about 10% higher than the result for sulfur in coal found in Problem I.7; sulfur emissions result from both coal and petroleum combustion, but not all the sulfur in either fuel is emitted to the atmosphere.

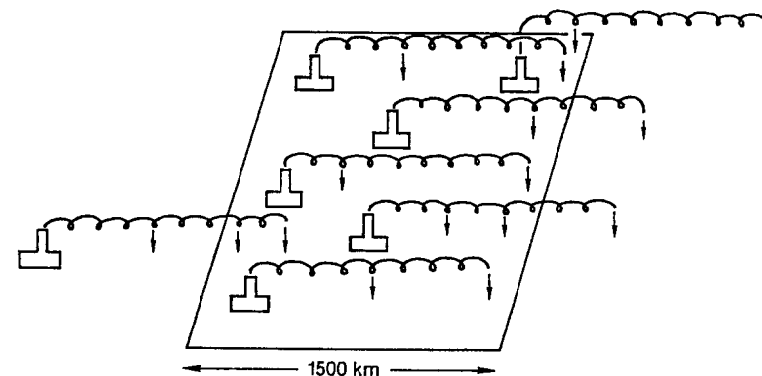


Figure II-4 Most, but not all, of the pollution that originates in a regional air shed will be deposited in it; most, but not all, of the pollution deposited in it also originated within its rough boundaries.

surface area. The SO₂ concentration in the region can be estimated as follows. The globally averaged SO₂ concentration due solely to anthropogenic SO₂ is roughly 85% of the natural background concentration, or $0.85 \times 0.20 \text{ ppb(v)} = 0.17 \text{ ppb(v)}$. If this is multiplied by the fraction of anthropogenic SO₂ produced in the Northeast (0.12) and divided by the fraction of Earth's area occupied by this air shed (0.002), an approximate regional concentration of SO₂ is obtained of 10.2 ppb(v). To strive for precision, the natural background of 0.20 ppb(v) of SO₂ might be added to this value, although such a correction is lost in a sea of uncertainty.

EXERCISE 1: We assumed, above, that the four-day residence time derived in Problem II.4 for remote sites was applicable to SO₂ in the atmosphere above the northeastern United States. If the residence time in dirty air were different from that in clean air, would you expect it to be longer or shorter? Why?

EXERCISE 2: As a very rough estimate of the likely SO₂ concentration in the atmosphere above densely populated urban areas, one could divide the percentage of total SO₂ emitted in the city by the percentage of Earth's surface area the city occupies. If that ratio were multiplied by 0.17 ppb(v), as above, would the resulting estimate be a reasonable one? Would it underestimate or overestimate the true answer? After you have tackled Problems 1 and 9 in Chapter III, you might want to return to this urban SO₂ problem and develop a better model.

6. A Polluted Lake

A stable and highly soluble pollutant is dumped into a lake at the rate of 0.16 tonnes per day. The lake volume is $4 \times 10^7 \text{ m}^3$ and the average water flow-through rate is $8 \times 10^4 \text{ m}^3/\text{day}$. Ignore evaporation from the lake surface and assume the pollutant is uniformly mixed in the lake. What eventual steady-state concentration will the pollutant reach?

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The rate at which pollution is added to the lake is given, so to calculate the steady-state stock, the residence time is needed. Because the pollutant is uniformly mixed in the lake, the residence time of the pollutant will equal the residence time of the lake water, which can be derived from the lake data provided. Dividing the stock of water, M_w , by the rate of water flow-through, F_w , the residence time of water in the lake, T_w , is obtained:

$$T_w = \frac{M_w}{F_w} = \frac{4 \times 10^7 \text{ m}^3}{8 \times 10^4 \text{ m}^3/\text{day}} = 500 \text{ days.} \quad (1)$$

Because the residence time of the pollutant, T_p , is equal to T_w , it follows that the steady-state stock of pollutant, M_p , is the pollution input rate, F_p , times the residence time, or:

$$M_p = F_p T_p = 0.16 \text{ tonnes/day} \times 500 \text{ days} = 80 \text{ tonnes.} \quad (2)$$

If we multiply the volume of a cubic meter of water by the density of water, we discover that a cubic meter of water weighs exactly one metric ton. Thus, the steady-state concentration of the pollutant is 80 tonnes/ (4×10^7) tonnes, or 2 parts per million (2.0×10^{-6}) by weight.

Aqueous concentrations are often specified in units of molarity, or moles per liter. Suppose the pollutant has a molecular weight of 40 (that is, there are a total of 40 protons and neutrons in the atoms of each molecule). Then the number of moles of pollutant is the weight in grams divided by 40, or $80 \times 10^6/40 = 2.0 \times 10^6$ moles. The number of liters of water in the lake is 4×10^{10} , so the molar concentration of the pollutant is 50×10^{-6} moles/liter. This is often written as 50 micromoles/liter, since a micromole is 10^{-6} moles. The unit of mole/liter is called a molar, and is sometimes designated by M. Thus the concentration can be expressed as $50 \times 10^{-6} \text{ M}$ or $50 \mu\text{M}$.

Now let us look at our two important assumptions. First, suppose that evaporation cannot be ignored, so the total rate at which water exits the lake now has two components: evaporation (one third) and stream outflow (two thirds) (see Figure II-5). The total rate at which water exits the lake is unchanged; it equals the inflow rate of $8 \times 10^4 \text{ m}^3/\text{day}$. Moreover, assume that the evaporating water is free of pollutant.⁵ Qualitatively, we would expect the steady-state concentration of pollutant to be higher now, because one possible exit pathway (with evaporating water) is closed off. The residence time of the pollutant is now no longer equal to that of the water but rather is given by the residence time associated only with stream outflow of water. This is given by

$$T_{w, \text{outflow}} = \frac{4 \times 10^7 \text{ m}^3}{5.3 \times 10^4 \text{ m}^3/\text{day}} = 750 \text{ days.} \quad (3)$$

The rest of the calculation remains the same, and the steady-state concentration of pollutant will be 3/2 greater than before.

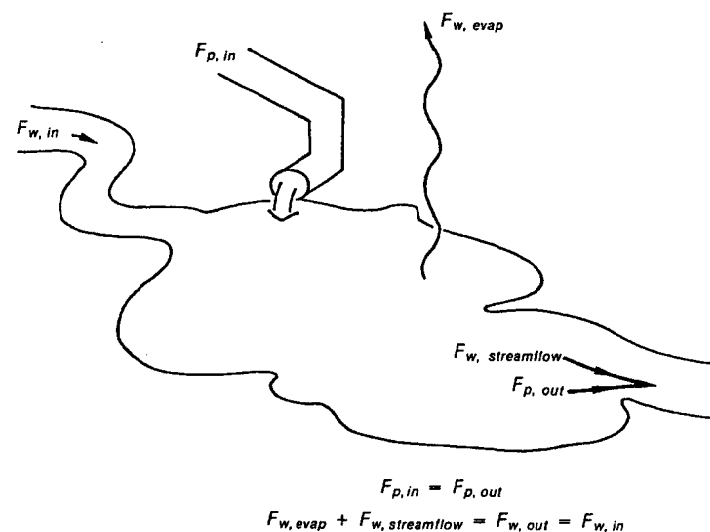


Figure II-5 The flows of pollution, F_p , and water, F_w , in and out of a polluted lake. It is assumed that the pollutant does not codistill with the evaporating lake water. The steady-state conditions for both pollutant and water are shown.

5. A substance that leaves the water with the evaporating vapor is said to "codistill." Some pollutants, like DDT, do codistill, but most do not.

The other fundamental assumption made in the original problem was that the pollutant uniformly mixes in the lake water. The effect of relaxing this assumption will depend on precisely how the pollutant is unevenly distributed within the lake and how water flows through the lake. An important special case, for example, is that of a stratified lake, in which the upper, warmer layer (epilimnion) is relatively isolated from the lower, colder layer (hypolimnion). Stratification is fairly common in late spring, summer, and early fall in deep lakes in regions with distinct warm and cold seasons [see Wetzel (1975) for a complete discussion of this phenomenon]. A pollutant entering the epilimnion of a stratified lake will not mix readily with the hypolimnionic water. Therefore, the *effective* dilution volume is the volume of the epilimnion rather than that of the whole lake, provided the residence time of the pollutant is short compared to the time constant characterizing the exchange of water between the two stratified layers.

EXERCISE 1: Assume that there is no transfer of water between the two layers during six months of the year when the lake is stratified. During the remaining six months, the lake is thoroughly and rapidly mixed. Assume the epilimnion occupies one fifth of the volume of the lake and that all the inflowing water and the incoming pollutant enter the lake at the surface in such a manner that during stratification they mix only with the epilimnion. Sketch, qualitatively, a graph of the concentration of pollutant as a function of time throughout the year at two depths: one midway down the epilimnion and one midway down the hypolimnion.

EXERCISE 2: Two lakes are located on the same river, as shown in Figure II-6. A is upstream of B. Water flows into A at a rate S_A ; it evaporates from A at a rate E_A and from B at a rate E_B . A tributary flows into the river between A and B at a rate S_B . Evaporation from the streams can be ignored. A soluble pollutant flows into lake

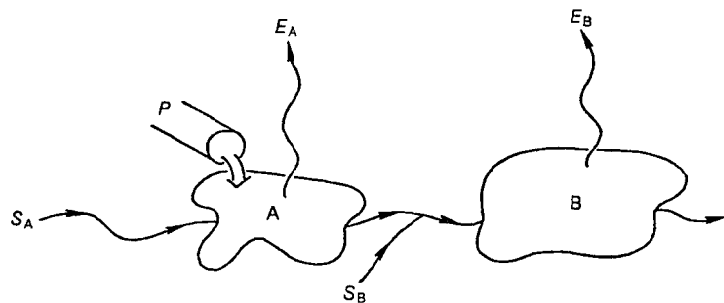


Figure II-6 Two lakes, A and B, on a stream. Lake A receives pollution directly, while B receives pollution from the outflow from A.

A at a rate P . There are no other sources of the pollutant, it is well mixed in both lakes, and it does not codistill. The lakes have water volume V_A and V_B , respectively, and are in hydrological steady states. (a) What is the rate of stream flow out of lake A? Into lake B? (b) What is the residence time of water in lake A? In lake B? (c) In the steady state, what concentration of pollutant will be found in each lake if P is given in units of grams per second, the S 's and E 's are in units of liters per second, and the V 's are in units of liters?

EXERCISE 3: If a substance can leave a box by several distinct exit pathways, as water leaves a lake either by evaporation or in an outflowing stream, then individual residence times can be associated with each exit process. Let $F_{out} = F_{out,1} + F_{out,2} + \dots + F_{out,n}$ and let the stock be M . Then the overall residence time, T , is equal to M/F_{out} . The individual residence times are given by $T_1 = M/F_{out,1}$, $T_2 = M/F_{out,2}$, . . . , $T_n = M/F_{out,n}$. Prove that $T^{-1} = T_1^{-1} + T_2^{-1} + \dots + T_n^{-1}$, and give an intuitive explanation of the meaning of these individual time constants. Is it correct to say that a molecule of the substance exiting by the i^{th} pathway will, on the average, have spent a time period T_i in the box before exiting? In Exercise 3 of Problem II.3, the residence times for carbon in leaves ($T_L = 1$ yr), wood ($T_W = 100$ yr) and the trees as a whole ($T_T = 15$ yr) do not satisfy the relation $T_T^{-1} = T_L^{-1} + T_W^{-1}$. Why not?

7. The Flow of Atmospheric Pollutants between Hemispheres

Ethane (C_2H_6) is a constituent of natural gas. It is emitted to the atmosphere whenever natural gas escapes unburned at wells and other sources, a process that constitutes the only major source of ethane in the atmosphere. The average concentration of ethane in the troposphere of the northern hemisphere, C_N , is roughly 1.0 ppb(v), and the average concentration in the southern hemisphere, C_S , is roughly 0.5 ppb(v). Ethane can exit from the troposphere by any of three mechanisms: passage to the stratosphere; chemical reaction resulting in transformation to other chemical species; and deposition to Earth's surface (for example, by washout from the atmosphere in rain or snow). It can also leave one hemisphere's troposphere by flowing to the other's. Assuming that the total exit rate from each hemisphere's troposphere is proportional to the concentration in the respective troposphere, and knowing that 3% as much natural gas escapes to the atmosphere unburned as is burned, estimate the net rate of ethane flow across the equator.⁶

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The data in this problem suggest a model with two boxes—one each for the atmospheres of the northern and the southern hemispheres. In problems of this type, a decision has to be made about whether to use as variables in the model the *amounts* or the *concentrations* of the substance studied. The two measures are interconvertible (amount equals concentration times the constant volume or mass of the medium) and so the correctness of the final answer will not depend on this decision, which is solely a matter of convenience. Inflows or emissions of substances are usually stated in units of amount per unit time, though, so I prefer to use amounts, not concentrations, as variables.

Figure II-7 shows the two tropospheric boxes with inflows, outflows, and stocks labeled. X_N and X_S refer to the amounts (or stocks) of ethane in the two boxes. Inflows E_N and E_S comprise ethane emis-

6. The values for C_N and C_S come from Singh et al. (1979). This problem illustrates how just a few experimental numbers can be used to estimate a very important parameter in environmental science—the interhemispheric flow of trace substances in the troposphere.

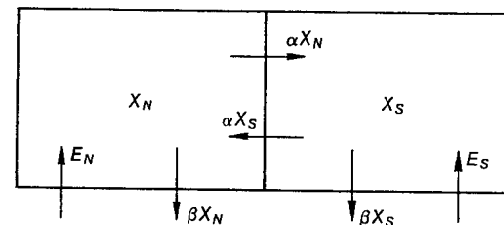


Figure II-7 The inflows and outflows of ethane in a two-box model of Earth's atmosphere. X_N and X_S are the amounts of ethane in the atmosphere above the northern and southern hemispheres, respectively. E_N and E_S are source terms, αX_N and αX_S describe flow across the equator, and βX_N and βX_S describe sinks within each box.

sions to the boxes from the ground. βX_N and βX_S are the total outflow rates from each box resulting from the three exit mechanisms mentioned in the problem statement. Finally, Figure II-7 separates the net interhemispheric flow into its two gross components—a flow from north to south labeled αX_N and a flow from south to north labeled αX_S . The net flow from north to south is the difference $\alpha(X_N - X_S)$.

The outflow rates, βX_N and βX_S , and the interhemispheric flow rates, αX_N and αX_S , are examples of "linear, donor-controlled flows" in which a rate of flow is simply proportional to the stock from which the flow originates. Intuition usually tells you when a flow is of this kind. In the case of deposition from the atmosphere to the ground, for example, each molecule of ethane falls independently of all the other molecules; thus the rate of deposition by fallout or washout when n molecules are present in the atmosphere ought to be half as great as that when $2n$ molecules are present. For ethane removal by chemical reaction, the situation is more complex. For example, if ethane reacts with a trace substance in the atmosphere, and if that substance is in short supply, then doubling the ethane concentration will not necessarily lead to a doubling of the reaction rate (see Exercise 6).

The convecting air that crosses the equator carries with it an amount of pollutant proportional to the amount of pollutant in the donor hemisphere. Thus, interhemispheric mixing is certainly a linear, donor-controlled process. Exit to the stratosphere should also be linear and donor-controlled. However, the inflow rates, E_N and E_S , are generally not proportional to the stocks. Polluters do not pollute in proportion to the amount of pollution present (at least not on purpose). If emissions *were* proportional to the stocks, the emission process would be called linear, receptor-controlled.⁷

In our case, $E_N + E_S$ is constant in time and independent of X_N and X_S . Its value can be determined using information in the problem

7. The exponential growth of a biological population results from linear, receptor-controlled inflow, as will be discussed below, in Chapter III, Section C.

statement and the Appendix. According to the Appendix (VII.2), natural gas was burned (in 1980) at a rate of 6×10^{19} J/yr, and the energy content of natural gas is 4×10^7 J/m³ (STP). Because one mole of any gas (STP) occupies 22.4 liters, there are 44.6 moles of gas in a cubic meter. Therefore, natural gas was burned at a rate, R , given by

$$\begin{aligned} R &= \frac{6 \times 10^{19} \text{ J/yr}}{4 \times 10^7 \text{ J/m}^3} \times 44.6 \text{ moles/m}^3 \\ &= 6.7 \times 10^{13} \text{ moles/yr.} \end{aligned} \quad (1)$$

Since natural gas escapes to the atmosphere at a rate equal to 3% of R , and since 6% (on a mole-per-mole basis) of natural gas is ethane (see Appendix [VII.3]),

$$\begin{aligned} E_N + E_S &= (0.03)(0.06)(6.7 \times 10^{13} \text{ moles/yr}) \\ &= 1.2 \times 10^{11} \text{ moles/yr.} \end{aligned} \quad (2)$$

We have determined only the sum of E_N and E_S . However, because nearly all natural gas is mined and vented in the northern hemisphere, we will assume, below, that $E_S = 0$ (but see Exercise 4).

To proceed, we must write the relations among the X 's and $E_N + E_S$, which we know, and α and β , which we want to know. To do this we write the steady-state equations, but we should be alert to the possibility that this is misleading. In particular, if $E_N + E_S$ is increasing rapidly enough with time, then X_N and X_S may also be increasing rapidly with time—in which case a steady-state model will be inadequate. Exercise 7 explores this possibility. For now, we ignore it.

The steady-state conditions on X_N and X_S are, respectively:

$$E_N + \alpha X_S = \alpha X_N + \beta X_N \quad (3)$$

and

$$E_S + \alpha X_N = \alpha X_S + \beta X_S. \quad (4)$$

These equations simply state that total inflow to each box (left-hand sides) equals total outflow (right-hand sides). Using this model, we can solve the problem.

If Eqs. 3 and 4 are added together,

$$E_N + E_S + \alpha X_S + \alpha X_N = \alpha X_N + \alpha X_S + \beta X_N + \beta X_S, \quad (5)$$

or

$$E_N + E_S = \beta(X_N + X_S). \quad (6)$$

This can be rewritten as

$$\beta = \frac{E_N + E_S}{X_N + X_S}. \quad (7)$$

Substitution of Eq. 7 into Eq. 3 yields a result for $\alpha(X_N - X_S)$, the interhemispheric flow rate:

$$\begin{aligned} \alpha(X_N - X_S) &= E_N - \frac{(E_N + E_S)X_N}{X_N + X_S} \\ &= \frac{E_N X_S - E_S X_N}{X_N + X_S} \end{aligned} \quad (8)$$

X_N and X_S can be determined from the known values of C_N and C_S by multiplying each concentration by the volume of the hemisphere's atmosphere. This is most easily done on a mole-per-mole basis (see the discussion in Problem II.4). From the Appendix we learn that the number of moles in the atmosphere is 1.8×10^{20} , so

$$\begin{aligned} X_N &= \frac{1.8 \times 10^{20} \text{ moles(air)}}{2 \text{ hemispheres}} \times 1 \times 10^{-9} \frac{\text{moles(ethane)}}{\text{moles(air)}} \\ &= 0.9 \times 10^{11} \text{ moles(ethane)}. \end{aligned} \quad (9)$$

Similarly,

$$X_S = 0.45 \times 10^{11} \text{ moles(ethane)}. \quad (10)$$

Substituting Eqs. 2, 9, and 10 into Eq. 8, and assuming $E_S = 0$, we determine the net rate of flow of ethane across the equator:

$$\alpha(X_N - X_S) = 0.40 \times 10^{11} \text{ moles/yr.} \quad (11)$$

EXERCISE 1: Express $\alpha(X_N - X_S)$ in units of tonnes/yr.

EXERCISE 2: The time constant, α^{-1} , characterizes interhemispheric mixing of air and its constituent trace gases. What is its value? Give an intuitive interpretation of this time constant.

EXERCISE 3: What is the value of the constant β^{-1} , which characterizes removal of ethane from either hemisphere?

EXERCISE 4: If the northern hemisphere were responsible for only 80% of all emissions, then at what rate would ethane flow across the equator and what would α^{-1} be? Given the information provided in the problem statement, how can you be sure that the northern hemisphere is responsible for at least two thirds of the ethane emissions?

* **EXERCISE 5:** Referring to Exercise 2 of Problem II.4, estimate what fraction of all the ethane exiting the troposphere does so by passing to the stratosphere.

* **EXERCISE 6:** Singh et al. (1979) emphasize the possibility that C_2H_6 is removed from the troposphere by chemical reaction with a reactive substance called a hydroxide radical, which is designated by the chemical symbol OH. OH is in such short supply in the atmosphere that the rate at which it reacts with C_2H_6 will depend on how much OH is present rather than on how much C_2H_6 is present. For an analogy, consider the number of beachcombers on a fairly crowded beach who find exotic shells. If the number of such shells washed ashore doubles, then so will the number of findings; but if the beach gets twice as crowded with beachcombers and the number of shells washed ashore remains constant, the number of findings will remain nearly constant. The beachcombers are like the C_2H_6 and the seashells washed ashore are like OH radicals. (a) If this C_2H_6 removal process is important, then because OH is likely to be rate-limiting, it is likely that the exit rate is independent of X_N and X_S . Recalculate the value of $\alpha(X_N - X_S)$, assuming both of the exit rates, βX_N and βX_S , are replaced by a common constant, $\beta_N = \beta_S$. Assume that $E_S = 0$. (b) The OH concentration in the southern hemisphere may exceed that in the northern hemisphere by about a factor of two because carbon monoxide, which removes OH from the atmosphere, is more abundant in the northern hemisphere's atmosphere. This would result in a greater exit rate in the south than in the north. Assuming $\beta_N = \frac{1}{2}(\beta_S)$ and $E_S = 0$, recalculate $\alpha(X_N - X_S)$.

* **EXERCISE 7:** If $E_N + E_S$ is growing at a rate of 2% per year, explain why the steady-state assumption should still yield a good approximation for α^{-1} and β^{-1} , given the present values of X_N and X_S .

8. A Perturbed Phosphorus Cycle (I)

The box model shown in Figure II-8 can be used to study phosphorus cycling in a lake. In the model, X_1 represents the amount of phosphorus (P) in living biomass, X_2 represents the amount of phosphorus in inorganic form, and X_3 represents the amount of phosphorus in dead organic material. Each X_i is in units of micromoles of phosphorus per liter of lake water. F_{ij} is the flow of phosphorus from stock i to stock j . In the steady state, $X_1 = 0.2$ micromoles(P)/liter, $X_2 = 0.1$ micromoles(P)/liter, $X_3 = 1.0$ micromoles(P)/liter, and the residence time of phosphorus in living biomass is 4 days. Assume that at time $t = 0$, the system is perturbed by the sudden addition of 0.02 micromoles(P)/liter to the inorganic phosphorus compartment, but the rate constants α , β , and γ remain unchanged. When a new steady state is reached, how much phosphorus will be in each compartment?

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Before calculating numbers, it is helpful to think about the structure of the model. The flows from X_1 to X_3 (resulting from death and excretion) and from X_3 to X_2 (resulting from decomposition) are assumed to be linear, donor-controlled processes. The flow from X_2 to X_1 is both donor- and receptor-controlled. Receptor-control results from the fact that the greater the biomass of living organisms, the greater will be the rate of inorganic phosphorus uptake by that biomass. In contrast, a large pool of inorganic phosphorus, X_2 , does not

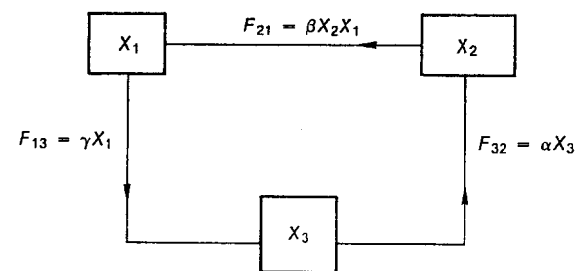


Figure II-8 The inflows and outflows in a three-box model of nutrient cycling.

cause more decomposition and thus does not increase the flow from X_3 to X_2 . Similarly, a large pool, X_3 , does not increase the death rate and hence does not result in a greater flow from X_1 to X_3 . Later on (Chapter III, Problems 10–15) we will discuss biological models that incorporate other assumptions about the dependence of inflows and outflows on compartment variables.

The first step in determining how the system responds to the perturbation of added phosphorus is to determine the numerical values of the rate constants α , β , and γ . Let the initial steady state be characterized by values of the X_i denoted \bar{X}_i . The steady-state conditions are derived by setting the inflow to each box equal to the outflow from that same box:

$$\beta\bar{X}_2\bar{X}_1 = \gamma\bar{X}_1, \quad (1)$$

$$\alpha\bar{X}_3 = \beta\bar{X}_2\bar{X}_1, \quad (2)$$

and

$$\gamma\bar{X}_1 = \alpha\bar{X}_3. \quad (3)$$

With numerical values for the \bar{X}_i substituted in, we get

$$0.02\beta = 0.2\gamma, \quad (4)$$

$$\alpha = 0.02\beta, \quad (5)$$

and

$$0.2\gamma = \alpha. \quad (6)$$

Eq. 6 can be derived from Eqs. 4 and 5 (just as Eq. 3 can be derived from Eqs. 1 and 2). Hence, Eq. 6 supplies no information⁸ not already contained in Eqs. 4 and 5. This redundancy means that Eqs. 4–6 do not provide enough constraints to determine the three rate constants. To determine them we have to use one more piece of information—the fact that the residence time of P in living biomass is 4 days. That residence time is the stock of P in living biomass, \bar{X}_1 , divided by the flow of P in or out in steady state, $\gamma\bar{X}_1$. So

$$\frac{\bar{X}_1}{\gamma\bar{X}_1} = 4 \text{ days}. \quad (7)$$

8. Redundancy of the steady-state equations follows from our assumption in Figure II-8 that the phosphorus flows in a closed cycle (i.e., prior to and also after the perturbation at $t = 0$, no phosphorus flows into any box from outside the system, and no phosphorus leaves the three-box system).

Combining Eq. 7 with Eqs. 4 and 5, it follows that

$$\gamma = (4 \text{ days})^{-1}, \quad (8)$$

$$\beta = (0.4 \text{ days})^{-1}[\text{micromoles(P)/liter}]^{-1}, \quad (9)$$

and

$$\alpha = (20 \text{ days})^{-1}. \quad (10)$$

Now we can solve the problem easily. Call the new values of the X_i , after the perturbation and after a new steady state is reached, \bar{X}'_i . The \bar{X}'_i must satisfy the same steady-state equations (Eqs. 1–3) satisfied by the \bar{X}_i , because the rate constants have not changed.

For the moment we will omit the cumbersome units of days and micromoles(P)/liter from our notation, but keep them in mind.

The new steady-state conditions are

$$\frac{\bar{X}'_1\bar{X}'_2}{0.4} = \frac{\bar{X}'_1}{4} \quad (11)$$

and

$$\frac{\bar{X}'_3}{20} = \frac{\bar{X}'_1\bar{X}'_2}{0.4}. \quad (12)$$

We will not bother writing the third steady-state equation because we now know the information in it can be derived from Eqs. 11 and 12. Eq. 11 tells us

$$\bar{X}'_2 = 0.1 \quad (13)$$

[in units of micromoles(P)/liter] and thus it hasn't changed at all. Eq. 12 then tells us

$$\bar{X}'_3 = 5\bar{X}'_1. \quad (14)$$

Finally, we can make use of the fact that the addition of phosphorus was 0.02 micromoles(P)/liter. Because phosphorus flows in a closed cycle, the total amount present initially plus the amount added to the system at $t = 0$ must equal the total amount present for all times subsequent to $t = 0$. Hence,

$$\begin{aligned} \bar{X}'_1 + \bar{X}'_2 + \bar{X}'_3 &= 0.02 + \bar{X}_1 + \bar{X}_2 + \bar{X}_3 \\ &= 0.02 + 0.2 + 0.1 + 1 \\ &= 1.320. \end{aligned} \quad (15)$$

Substituting Eqs. 13 and 14 into Eq. 15,

$$\bar{X}_1 + 0.1 + 5\bar{X}_1 = 1.320, \quad (16)$$

or

$$\bar{X}_1 = \frac{1.220}{6} = 0.203 \text{ micromoles(P)/liter}; \quad (17)$$

and, by Eq. 15,

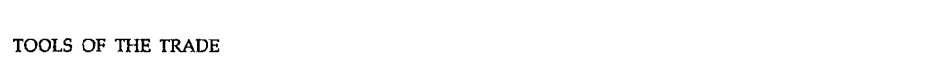
$$\bar{X}_3 = 1.017 \text{ micromoles(P)/liter}. \quad (18)$$

Note that our answer is independent of where the extra phosphorus was initially placed. Why was it the case that $\bar{X}_i = \bar{X}_i$ only for $i = 2$? The clue to this is Eq. 1, which tells us that in the steady state, X_2 is a constant equal to γ/β .

EXERCISE 1: Give a qualitative explanation of why the flow from X_2 to X_1 could be assumed to be proportional to the product of X_1 and X_2 while the other flows are simply donor controlled (see Problem II.7)?

* **EXERCISE 2:** The conversion of phosphorus from organic to inorganic form is carried out by an enzyme called phosphatase. Suppose the initial perturbation at $t = 0$ had been a change in the rate constant governing this conversion. In particular, assume that a permanent 10% reduction in α occurred because a phosphatase inhibitor was dumped into the lake (acid rain could cause such inhibition). When a new steady state is reached, how much phosphorus will be in each compartment?

* **EXERCISE 3:** Termites process about 13×10^9 tonnes of carbon per year,⁹ removing it from dead organic matter and returning it to the atmosphere in the form of CO_2 . If Earth's termite populations are destroyed and no other decomposer organisms fill their niche, by how much would the amount of carbon in the atmosphere, in living terrestrial vegetation, and in dead terrestrial organic matter change? You may assume a box model of the same form as the phosphorus model, with X_1 , X_2 , and X_3 referring to the amounts of carbon in living terrestrial vegetation, the atmosphere, and dead terrestrial organic matter, respectively. Ignore any changes in the amount of carbon in the oceans or in the rate of exchange of carbon between the oceans and the atmosphere. You may also assume that the decrease



in decomposition activity upon the demise of the termites is reflected in a proportional decrease in the rate constant α . The Appendix (XIII.1,5) provides the information needed to determine numerical values for the \bar{X}_i and for α , β , and γ for the carbon cycle.

9. Zimmerman et al. (1982) present the results of some fascinating research on the immense ecological role of termites.

9. Where Would All the Water Go?

If evapotranspiration from Earth's land area were to diminish by 20% uniformly over the land area, as might result from widespread removal of vegetation, what changes would occur in the globally averaged precipitation on the land surface and in the globally averaged runoff from the land to the sea?

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Because we need not consider stocks or time constants, this is not a residence-time problem. It is a box-model problem, however, requiring careful identification of boxes and balancing of inflows and outflows for each box. An immediate guess might be that precipitation would decrease by 20%; but this would be correct only if the hydrocycle did not link our two boxes, the continents and the seas. The existence of runoff from the land to the sea implies that some evaporation from the sea falls as precipitation on the land. Because this portion of land precipitation will not be affected by the 20% decrease in evapotranspiration from the land, the overall effect will be less than 20%.

To solve the problem, a systematic look at the global water budget is helpful. The following water flow rates can be defined:

- P_L = rate of precipitation on the land
- P_S = rate of precipitation on the sea
- R = rate of runoff from the land to the sea
- E_{LL} = rate of evapotranspiration from the land that falls as precipitation on the land
- E_{LS} = rate of evapotranspiration from the land that falls as precipitation on the sea
- E_{SS} = rate of evaporation from the sea that falls as precipitation on the sea
- E_{SL} = rate of evaporation from the sea that falls as precipitation on the land

These flows are illustrated in Figure II-9.

Our problem can now be restated in terms of these definitions: How will R and P_L change if E_{LL} and E_{LS} both diminish by 20%? There are three water-conservation relations among the seven quantities we have defined. The first relation states that water is conserved in the sea:

$$P_S + R = E_{SS} + E_{SL}. \quad (1)$$

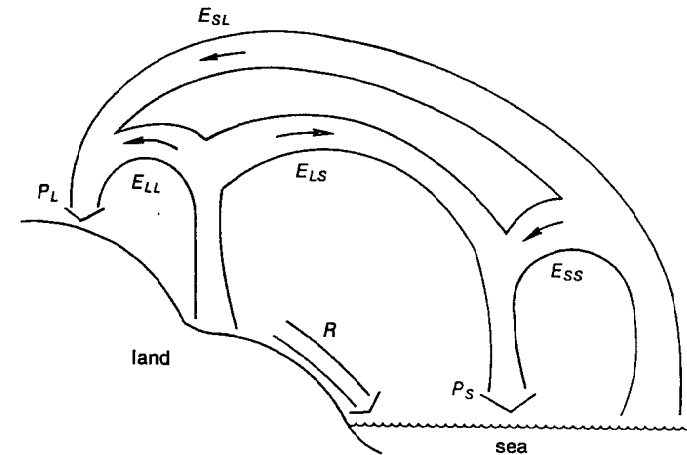


Figure II-9 The flows of water in the global hydrocycle.

The second states that water is conserved on land:¹⁰

$$P_L = R + E_{LL} + E_{LS}, \quad (2)$$

and the third states that the rate of water flow from land to sea equals the rate from sea to land:

$$R + E_{LS} = E_{SL}. \quad (3)$$

Any two of these can be derived from the third plus the two identities that follow from the definitions:

$$P_L = E_{LL} + E_{SL}, \quad (4)$$

and

$$P_S = E_{SS} + E_{LS}. \quad (5)$$

All told, there are three independent relations among the seven quantities. Thus, four independent empirical values are needed to determine all seven quantities.

In the Appendix (VI.3), values for P_L , P_S , and R are given. The fourth piece of information we need is that approximately 25% of the evapotranspiration from the land precipitates on the sea, while 75%,

10. This equation is correct only if the stock of groundwater is unchanged. Exercise 2 asks you to examine this assumption.

or three times as much, precipitates on the land ($E_{LL} = 3E_{LS}$). (Exercise 4, below, suggests a procedure for deriving this estimate of the ratio of E_{LL} to E_{LS} . The value of 3 given here is only approximate; a precise empirical value is not available.) With this information and the equations above, we obtain the following values: $P_L = 108 \times 10^3 \text{ km}^3/\text{yr}$; $P_S = 410 \times 10^3 \text{ km}^3/\text{yr}$; $R = 46 \times 10^3 \text{ km}^3/\text{yr}$; $E_{LL} = 46.5 \times 10^3 \text{ km}^3/\text{yr}$; $E_{LS} = 15.5 \times 10^3 \text{ km}^3/\text{yr}$; $E_{SS} = 394.5 \times 10^3 \text{ km}^3/\text{yr}$; and $E_{SL} = 61.5 \times 10^3 \text{ km}^3/\text{yr}$. As you may suspect, non-significant figures have accumulated here; we can drop them later.

If the reduction in evapotranspiration is uniformly distributed over the land, it is reasonable to assume that E_{LL} and E_{LS} each decrease by 20%. (Note, on the other hand, that if the decrease in evapotranspiration occurred primarily along the coastlines of the continents, then this assumption would be a poor one.) Using primed quantities (P'_L , P'_S , R' , etc.) to denote the rates subsequent to the 20% decrease in evapotranspiration, we can write

$$\begin{aligned} E'_{SS} &= E_{SS}, \\ E'_{SL} &= E_{SL}, \\ E'_{LL} &= .8 E_{LL}, \end{aligned} \quad (6)$$

and

$$E'_{LS} = 0.8 E_{LS}.$$

Then, setting up new conservation equations and identities for the primed quantities, the primed versions of Eq. 3 and 4 become:

$$R' = E'_{SL} - E'_{LS} \quad (3')$$

and

$$P'_L = E'_{LL} + E'_{SL}. \quad (4')$$

Use of Eq. 6 then leads to

$$R' = E_{SL} - 0.8 E_{LS}, \quad (7)$$

$$P'_L = 0.8 E_{LL} + E_{SL}. \quad (8)$$

Using Eqs. 3 and 4, these can be rewritten as

$$R' = R + 0.2 E_{LS} \quad (9)$$

and

$$P'_L = P_L - 0.2 E_{LL}. \quad (10)$$

Numerically, $R' = (46.0 + 3.10) \times 10^3 \text{ km}^3/\text{yr}$, which is about a 7% increase over R ; and $P'_L = (108 - 9.30) \times 10^3 \text{ km}^3/\text{yr}$, which is about a 9% decrease from P_L .

Some readers will be able to solve this problem without plodding through all the formal steps presented here. It is helpful to see how to formalize problems like this one, however, because more complicated situations often make this approach necessary.

EXERCISE 1: By how much will the total global precipitation rate change?

* **EXERCISE 2:** Changes in hydrologic flows will result in changes in stocks and/or residence times. If the residence times for water in each of the major water compartments on Earth (atmosphere, ocean, ice, soil moisture, groundwater, lakes, and streams) are unchanged as a result of the changes in the flows worked out above, try to deduce which stocks of water will increase, which will decrease, and which will stay the same. For each compartment, would you expect residence time or stock of water to remain more nearly constant subsequent to the changes in flows?

* **EXERCISE 3:** A reduced rate of precipitation on the land, resulting directly from reduced transpiration, may lead to a reduction in plant growth. On the other hand, reduced transpiration may lead to more moist soil, perhaps enhancing plant growth. Either of these changes in plant growth will alter the transpiration rate again. Such a circular chain of events is called a feedback process. Our solution to the main problem, above, was deficient because it neglected feedback effects. Another feedback process that can result from a decreased evapotranspiration rate is a decreased rate of latent heat transfer from the surface upwards, thus increasing both surface temperature and evaporation rate. Removal of vegetation could induce other climate changes, including an increased CO_2 greenhouse warming and an altered radiation balance caused by changes in the surface albedo (reflectance) of the devegetated land. An increased atmospheric CO_2 concentration would probably further decrease the rate at which plants transpire water.

These effects will be discussed quantitatively in subsequent problems (III.7,8), but for now try to describe the qualitative nature of these feedback effects on P'_L . An amusing wrinkle to consider is that with increased runoff the amount of water in the sea would rise, thus increasing its surface area. Would this significantly increase the rate of evaporation from the sea and thus alter our answer?

* **EXERCISE 4:** Using (a) the residence time for atmospheric water derived in Problem II.2 and (b) a map of the world, estimate the ratio of E_{LL} to E_{LS} .

EXERCISE 5: Deforestation of mountain slopes has been proposed as a way to provide more runoff water for irrigation in the western United States.¹¹ The idea is that more snowmelt will flow into reservoirs while less will be transpired away by trees. Is this a sensible idea?

10. Aluminum in the Himalaya

In a remote area in Nepal, the concentration of aluminum (Al) in outdoor air at ground level averages $9.4 \times 10^{-8} \mu\text{g}/\text{cm}^3$. (It is much higher inside the Sherpa dwellings because of wood and yak dung burning).¹² At the same site, the Al concentration in the top 1 cm of fresh snow averages $0.12 \mu\text{g}/\text{g}$, while in the top 1 cm of three-day-old snow it averages $0.20 \mu\text{g}/\text{g}$. (a) Calculate the average deposition velocity of the Al falling to the ground when it is not snowing. (b) How large are the particles to which the falling aluminum is attached?

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(a) This is a variation on the usual stock-flow-residence time problem. You are given a stock, expressed as the concentration of aluminum in the air. A flow of aluminum groundward can be derived from the information about old snow and new snow if you assume that the extra aluminum on the old snow surface is due to deposition. Now, however, you are asked to calculate a deposition velocity rather than a residence time. The reason a deposition velocity and not a residence time can be calculated from the given data is that the stock of aluminum in the atmosphere is expressed in units of mass per unit volume ($\mu\text{g}/\text{cm}^3$) while the flow (see below) must be calculated in units of mass per unit time per unit area. Dividing the flow by the stock gives a quantity expressed in units of length per unit time. This quantity is not an inverse residence time but, rather, a deposition velocity.

The flow can be calculated as $0.20 - 0.12 = 0.08 \mu\text{g}$ of Al per gram of snow per 3 days (see Figure II-10). This is the rate of increase of aluminum concentration in the top centimeter of snow. Since fairly fresh snow has a density of about $0.1 \text{ g}/\text{cm}^3$ (about 0.1 that of water), the aluminum was measured in $0.1 \text{ g}(\text{snow})/\text{cm}^2$ of surface. Hence, the flow can be expressed as

$$F = \frac{0.08 \frac{\mu\text{g}(\text{Al})}{\text{g}(\text{snow})} \times 0.1 \frac{\text{g}(\text{snow})}{\text{cm}^2}}{3 \text{ days}} \quad (1)$$

$$= 0.0027 \mu\text{g}(\text{Al})/\text{cm}^2 \text{ day}.$$

11. See, for example, the collection of articles on this topic in *The Water Resources Bulletin*, Volume 19, June, 1983.

12. The data and the inspiration for this problem come from Davidson et al. (1981).

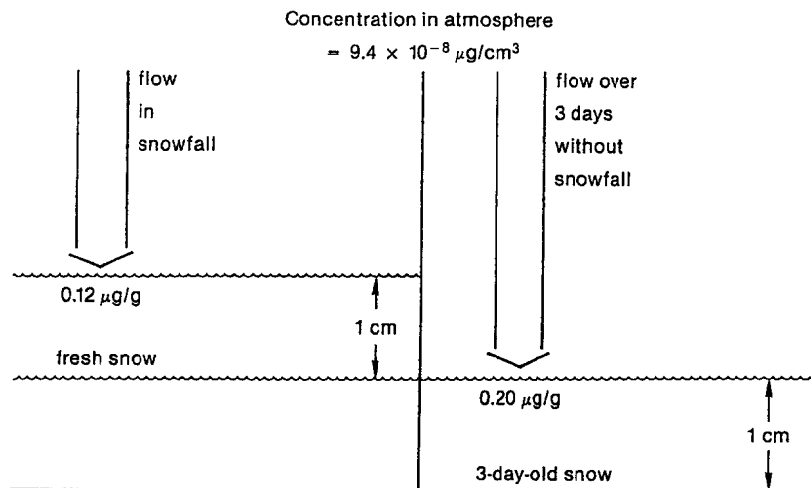


Figure II-10 A pictorial summary of the input data given in the problem statement.

The stock in the atmosphere is

$$M = 9.4 \times 10^{-8} \mu\text{g(Al)/cm}^3. \quad (2)$$

Hence, the deposition velocity, F/M , is

$$\begin{aligned} \frac{F}{M} &= 2.9 \times 10^4 \text{ cm/day} \\ &= 0.34 \text{ cm/sec.} \end{aligned} \quad (3)$$

(b) To calculate the size of the particles falling at this speed, a digression is needed. Stokes Law describes the rate at which objects fall through a medium like air or water, provided the velocity of the object is small enough to create no turbulence. The law states that the frictional drag force on a spherical object is

$$F = 6\pi\eta vr, \quad (4)$$

where η is the viscosity of the medium (given in the Appendix V.1), v is the velocity, and r is the object's radius.¹³ Stokes Law is applicable provided a certain quantity called the Reynolds number, R , defined by

$$R = \rho_m vr / \eta, \quad (5)$$

13. For a nonspherical object, r is replaced by an effective radius. Consult a physics text for details.

is less than about 0.5. Here, ρ_m is the density of the medium; in this case, the medium is air, so $\rho_m \approx 0.001 \text{ g/cm}^3$. A falling object soon reaches a terminal velocity in which the frictional force retarding its motion equals the gravitational-minus-buoyancy force pulling it downward. For a particle falling through air the buoyancy is negligible and so the downward force is the product of the mass, m , times the acceleration of gravity, g . Hence the terminal velocity can be calculated by setting

$$6\pi\eta vr = mg. \quad (6)$$

This balance of forces is illustrated in Figure II-11.

We know the values of everything in Eq. 6 except r and m . Assuming the particles to which the aluminum is attached are spherical, r is their average radius; m is their average mass. It is a reasonable assumption that the density of the particles, ρ_p , is very roughly equal to 1 g/cm^3 , the density of water. This is because small particles falling from the atmosphere are often actually aerosols. Aerosols may contain water; but even if dry, they are comprised of fluffy solids—irregular hollow structures less dense than typical solid materials forming Earth's crust. Thus, we find

$$m = \frac{4}{3}\pi r^3 \rho_p. \quad (7)$$

Rewriting Eq. 6 yields

$$6\pi\eta vr = \frac{4}{3}\pi r^3 \rho_p g \quad (8)$$

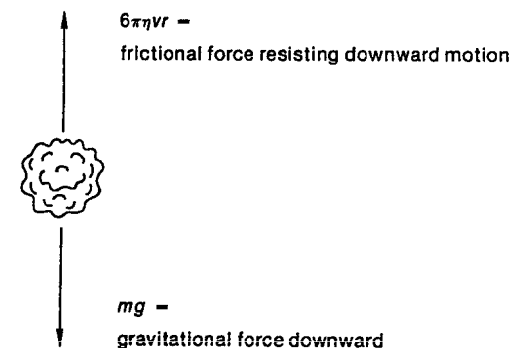


Figure II-11 The forces acting on a small particle in the atmosphere; v , r , and m are the particle's velocity, radius, and mass, respectively, η is the viscosity of air, and g is the acceleration of gravity.

109