More on Residence Times and Half-lives

Residence times (τ) can be determined for the water in a particular reservoir (such as a lake) or for a substance within it (such as a contaminant in a lake). The residence time for water in a reservoir can be determined from the total amount (the stock - usually expressed as a mass or volume) of the reservoir and either the total rate of inflow (expressed in units of mass or volume per time) or outflow. Similarly, the residence time for any substance in a reservoir can be determined. *Note: units of the numerator and denominator must be consistent in order to yield a dimension of time for the ratio*.

$$\tau = \frac{M}{F} = \frac{\text{stock of a substance in reservoir}}{\text{flow rate in/out}}$$

If a pollutant is non-volatile, stable and highly water soluble it will have a residence time similar to that of the water itself assuming no water loss via evaporation (i.e., $\tau_p \sim \tau_w$). However, if the water is lost from the reservoir via a pathway not available to the pollutant (such as evaporation), then $\tau_p > \tau_w$. It is also possible that a pollutant has loss pathways not available to the water (such as degradation or sedimentation). It this case, τ_p must be less than τ_w.

The *residence time* of a substance within a reservoir may be governed not only by the residence time of the water in the reservoir itself (essentially a dilution or flushing factor), but also by a variety of physical, chemical and biological processes, which most often follow first order or pseudo-first order kinetics. Since the stock of a pollutant can also be expressed as a concentration ([C]) and it's rate of loss (dC/dt) can be written as the product of a rate constant (k) and concentration ([C]);

$$\tau_p = \frac{[C]}{k[C]} = \frac{1}{k}$$

or if the pollutant can be lost by several first order processes,

$$\tau_p = \frac{[C]}{\Sigma \text{ rates}} = \frac{[C]}{\Sigma k_i[C]} = \frac{1}{\Sigma k_i}$$

where one of the rate constants is $k_w = 1/\tau_w$ is due simply to the residence time of the water in the reservoir.

For first order (or pseudo-first order) processes, the rates can be expressed as k [C], where k is the first order (or pseudo-first) order rate constants (units = time^{-1}). Recall that for a first order process, the rate (d[C]/dt) = - k [C]^1

Collecting like terms and integrating yields,

$$\int \frac{d[C]}{[C]} = -k \int dt \qquad\qquad \ln[C] \Big|_{Co}^{Ct} = -kt$$

or

$$[C]_t = [C]_o\, e^{-kt}$$

So at t = τ, $[C]_t = [C]_o\, e^{-1}$

and the concentration has dropped to $1/e^{th}$ of it's original value. Hence, the *residence time* is actually the time required for the stock to drop to $1/e$ ($1/2.718 = 0.368$) of it's original value if all inputs were to immediately cease. So a non-volatile persistent contaminant, which does not otherwise breakdown, would be diluted to 37% of its original concentration in period of one residence time (assuming the contaminant is evenly distributed in a thoroughly mixed reservoir with negligible evaporation).

The *half-life* ($t_{1/2}$) is the amount of time required for the stock to drop by 50%. Hence, to calculate the amount of material remaining after some time, one can use the integrated for of the rate equation (above) or apply the following relation;

$$[C]_t = [C]_o(\tfrac{1}{2})^n$$

where $[C]_t$ is the concentration after some time (t), $[C]_o$ is the initial concentration and n is the number of half-lives. As you would expect, after one half-life the concentration will be $[C]_o$ $(\tfrac{1}{2})^1$ or one half of its original value. After two half-lives, the concentration will be $[C]_o$ $(\tfrac{1}{2})^2$ or one quarter of its original value and so on. This works equally well for non-integer values of n.
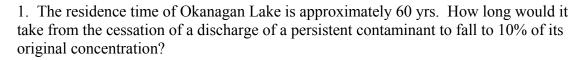
Although the residence time is easier to directly estimate with the knowledge of process rates or rate constants, the half-life is often easier to interpret.

Since, $\tau = 1/k$
where k is the first order rate constant,
and $t_{1/2} = \ln 2/k$
it can be shown that;
            $t_{1/2} = \tau\,(\ln 2) = 0.693\ \tau$

Hence, the half-life is roughly 70% of the lifetime.

Examples:

1. The residence time of Okanagan Lake is approximately 60 yrs. How long would it take from the cessation of a discharge of a persistent contaminant to fall to 10% of its original concentration?

[Ans: 140 yr]

2. If the concentration of a pollutant in Lake Superior were 1.0 ppm today, how many half lives would it take for its concentration to fall to 50 ppb ppm if all input of the pollutant into the lake ceased immediately?

[Ans: 4.3]

3. A compound has a chemical degradation rate constant of 6.6×10^{-3} s^{-1} in a 2500 m^3 water treatment plant. At what flow rate could the treatment plant be operated if a 10 minute water contact time is required to remove this compound?

[Ans: 1.8 x 10^6 m^3 day^{-1}]

4. A soluble pollutant is dumped into a lake starting on day zero. The rate constant of the increase is 0.069 day^{-1}. The integrated rate equation is given by $[C]_t/[C]_{max} = (1 - e^{-kt})$. Sketch a labeled plot of the relative concentration over the first 60 days. What fraction of the steady state concentration is reached after 35 days?

[Ans: 0.91]

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 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 (τ)*. Thus, if the 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 τ be the residence time, then $\tau = M/F_{in} = M/F_{out}$.

A Polluted Lake Problem[1]

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 x 10^7 m^3 and the average water flow-through rate is 8 x 10^4 m^3/day. Ignore evaporation from the lake surface and assume the pollutant in uniformly mixed in the lake. What eventual steady-state concentration will the pollutant reach?

Solution
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, τ_w is obtained:

$$\tau_w = \frac{M_w}{F_w} = \frac{4 \times 10^7 \text{ m}^3}{8 \times 10^4 \text{ m}^3 / \text{day}} = 500 \text{ days}$$

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

$$M_p = F_p \tau_p = 0.16 \text{ tonnes/day x } 500 \text{ days} = 80 \text{ tonnes}$$

If we multiply the volume of a cubic meter of water by the density of water, we discover that 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 x 10^7) tones, or 2 parts per million (2.0 x 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 x 10^6/40 = 2.0 x 10^6 moles. The number of liters of water in the lake is 4 x 10^{10}, so the molar concentration of the pollutant is 50 x

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[1] Adapted from Consider a Spherical Cow:
    A course in Environmental Problem Solving, John Harte, University Science Books, CA 1988

10^{-6} miles/liter. This is often written as 50 micromoles/liter, since a micromole is 10^{-6} moles. The unit of the mole/liter is called a molar, and is sometimes designated by M. Thus the concentration can be expressed as $50 \times 10^{-6} M$ or $50 \ \mu M$.

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). The total rate at which water exits the lake is unchanged; it equals the inflow rate of $8 \times 10^4 \ m^3$/day. Moreover, assume that the evaporating water is free of pollutant.[2] 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

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

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

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. A pollutant entering the epilimnion of a stratified lake will not mix readily with the hypolimnionic water.

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[2] A substance that leaves the water with the evaporating vapour is said to "codistill." Some pollutants, like DDT, do codistill, but most do not.

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: A pollutant enters a thermally stratified lake by two distinct pathways. A river delivers the pollutant into the epilimnion at a rate of 35 kg/yr, whereas groundwater seepage delivers the pollutant to the hypoliminion at 4 kg/yr. Because of sedimentation, the residence time of the pollutant in the lower layer is 1.5 yrs. The average concentration in the whole lake is 80 ng/L, the total lake volume is 10^9 m^3 and everything is at steady state.
a) Draw a diagram of the system illustrating stocks and fluxes, where possible.
b) What is the total amount of pollutant in the lake?
c) Set up equations relating stocks, flows and residence times.
d) Solve for the residence time of the pollutant in the upper layer?

    EXERCISE 3: Two lakes are located on the same river, as shown in the Figure (below). 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 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 unites of liters per second, and the V's are in units of liters?

Non-Steady-State Box Models

The previous problems were solved by equating compartment inflows to compartment outflows. This was appropriate because the problems involved steady-state situations. A more difficult class of problems involves stocks that change over time, a situation arising when inflows are not in balance with outflows. When the inflow, F_{in}, is not equal to the outflow, F_{out}, then the rate of change of the stock is given by

$$\text{rate of change of } M \;=\; F_{in} \;-\; F_{out} \tag{1}$$

If $F_{in} > F_{out}$, M increases with time; while if $F_{in} < F_{out}$, M decreases. In either case, there is no longer a well-defined residence time.

Eq. 1 is the starting point for many non-steady state box models.

If the flows are known functions of the stock, then the equation can be solved for $M(t)$. The problems in this section illustrate how this is done for the case in which the stocks vary smoothly, so that a differential equation can be written.

$$\frac{dM}{dt} = F_{in} - F_{out} \tag{2}$$

In a multi-box model, a *set* of equations like Eq. 1 results. If the flow in or out of one box depends upon the stocks in that box and also the stocks in other boxes, then a set of interconnected, or coupled, equations results.

Pollution Buildup in a Lake

A lake has a volume of 10^6 m^3 and a surface area 6 x 10^4 m^2. Water flows into the lake at an average rate of 0.005 m^3/sec. The amount of water that evaporates yearly from the lake is equivalent in volume to the lake's top meter of water. Initially, the lakewater is pristine, but at a certain time a soluble, non-codistilling pollutant is discharged into the lake at a steady rate of 40 tonnes/yr. Derive a formula for the concentration of pollutant in the lake as a function of time since the pollutant discharge began.

Solution
A noncodistilling pollutant is a substance that does not evaporate away with evaporating water. Therefore, evaporation of lakewater is not an exit pathway for the pollutant. However, if the lakewater flows out of the lake in an outlet stream or via underground seepage, that water outflow will remove pollutant. So to begin, let's calculate the stream and seepage outflow rate for the lakewater. The lakewater is in a steady state, with stock, M_w, equal to 10^6 tonnes (H$_2$O) (since 1 m^3 of water has a mass of 1 tonne). The water inflow rate, F_w, is 0.005 tonnes(H$_2$O)/sec $=$ 1.6 x 10^5 tonnes(H$_2$O)/yr and therefore the total water outflow rate must also equal 1.6 x 10^5 tonnes(H$_2$O)/yr. The evaporation

outflow rate is 1 m/yr times the area of the lake, or 0.6×10^5 tonnes(H_2O)/yr, and hence the stream and seepage outflow rate is 10^5 tonnes(H_2O)/yr.

At any time, t, let $M_p(t)$ equal the mass of pollutant in the lake in units of tonnes. The concentration of pollutant at time t is $M_p(t)/M_w$ in units of tonnes(pollutant)/tonne(water). If the stream-plus-seepage outflow rate is multiplied by the concentration of pollutant outflow, $F_{p,out}(t)$, is obtained:

$$F_{p,out} = 10^5 \frac{M_p}{M_w} \quad (3)$$
$$= 0.1\, M_p$$

in units of tonnes(pollutant)/yr.

The rate at which pollutant flows into the lake, $F_{p,in}$, equals 40 tonnes(pollutant)/yr. Equating the rate of change of M_p to the net difference between inflow and outflow,

$$\frac{dM_p}{dt} = F_{p,in} - F_{p,out} \quad (4)$$
$$= 40 - 0.1\, M_p,$$

with M_p in units of tonnes(pollutant) and time in units of years. This equation is of the form,

$$\frac{dX}{dt} = a + bX \quad (5)$$

and has a general solution[3]

$$X(t) = \frac{-a}{b} + ce^{bt}. \quad (6)$$

The constant, c, must be determined from a specified condition on $X(t)$. Thus if $X(0)$ is a known amount, the relation

$$X(0) = \frac{-a}{b} + c, \quad (7)$$

which follows from Eq. 6, determines the unknown constant, c.

In our case, $a = 40$, $b = -0.1$, and if $t = 0$ is the time the pollutant discharge began, then $X(0) = 0$. Therefore, $c = a/b$. In units of tonnes, the mass of pollutant in the lake is given by

$$M_p(t) = \frac{40}{0.1} - \frac{40}{0.1} e^{-0.1t}. \quad (8)$$

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[3] You can derive the general solution by rewriting Eq. 3 in the form $dX/(a + bX) = dt$ and integrating both sides. You can also verify that Eq.6 is correct by direct substitution into Eq. 5.

EXERCISE 1: What amount and what concentration of pollutant will exist in the lake as *t* approaches infinity?

EXERCISE 2: Since the water in the lake is in steady state, its residence time τ_w, can be computed. What is the value of that residence time? As *t* approaches infinity, the pollutant approaches a steady state; therefore a residence time, τ_p, is derivable. What is the value of that residence time? Explain why τ_p is greater than τ_w, and interpret the difference τ_w^{-1} - τ_p^{-1}.

EXERCISE 3: Draw a plot of Eq. 6 to get a visual sense of how pollution builds up in a lake. Include values of *X(t)* at 2-year intervals for a 20-year period starting at *t* = 0.