Lecture 15/16: Catchment Hydrogeochemistry

- What is a spherical cow?
- Mass balance models
- Kinetics of mass balance models
- Treating a catchment as a black box

Spherical cow – a highly simplified scientific model of complex real life phenomena

- Purpose is to reduce a complex system into major components that can be easily modeled
- Useful start to understanding observations in earth systems science
- Often involves "back of the envelope" calculations

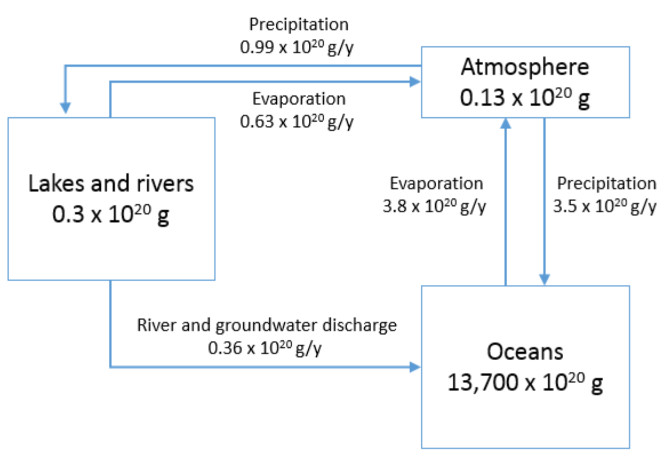
Mass balance model – a model that accounts for conservation of mass in a physical system

- ***Reservoir*** **(M_i)** – a defined space containing a certain mass of a component of interest *i*
- ***Flux*** **(F_i)** – transfer of component *i* into (F_{in}) or out of (F_{out}) a reservoir
- ***Steady-state*** – describes a system where the amount of component *i* in a reservoir does not change with time (fluxes are balanced)
- ***Residence time*** **(τ_i)** – under steady-state conditions, the average amount of time a molecule of the component *i* spends in a reservoir; calculated as the reservoir mass divided by input OR output fluxes

Example 1:
A one reservoir (box) system with two fluxes of component *i*: $F_{i,\mathrm{in}} \rightarrow [M_i] \rightarrow F_{i,\mathrm{out}}$
Assuming the reservoir is at steady-state with respect to *i*, if $F_{i,\mathrm{in}}$ = 5 mol/y and M_i = 500 mol, what is the residence time of substance *i* in the reservoir? (= 100 y)

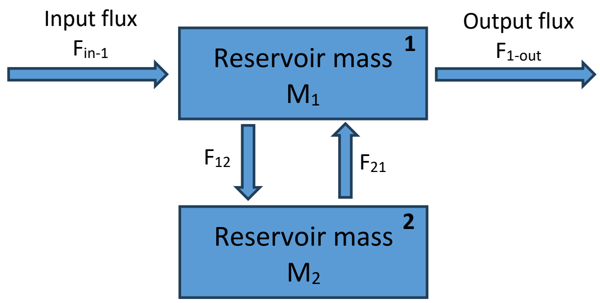
Example 2: A three-box system:

The Hydrologic Cycle: Simple Box Model for Water



What is the residence time of water in the atmosphere, assuming that the atmosphere is at steady state with respect to the mass of water? (= 0.029 y = 10.7 days)

Kinetics of Mass Balance models
Here is a system with two boxes and fluxes connecting them



- dM_i/dt = the change in mass of *i* in the system
  - $dM_i/dt = \Sigma F_{in} - \Sigma F_{out} \pm R$ (biogeochemical production or consumption of *i* in the reservoir)
  - At steady-state, $dM_i/dt = 0$; M_i and F_i are constant
  - For M1 at steady-state: $F_{1\text{-in}} + F_{21} = F_{12} + F_{1\text{-out}}$
  - For M2 at steady-state: $F_{12} = F_{21}$
  - For M1 not at steady-state: $dM_i/dt = (F_{1\text{-in}} + F_{21}) - (F_{12} + F_{1\text{-out}})$
  - For M2 not at steady-state: $dM_i/dt = F_{12} - F_{21}$

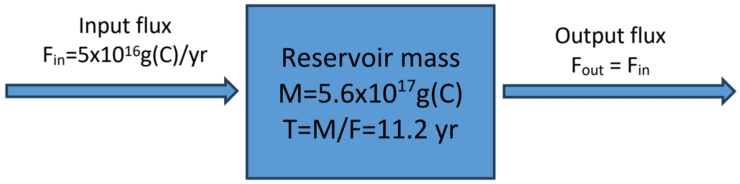
First-order kinetics

- fluxes can be constant values, or they can depend on factors such as the mass of the reservoir
  - $F = kM$, where k is a first-order rate constant
  - Indicates the fraction by which a reservoir increases or decreases in a given time frame
  - These relationships can be used to derive changes in M_i if fluxes are known

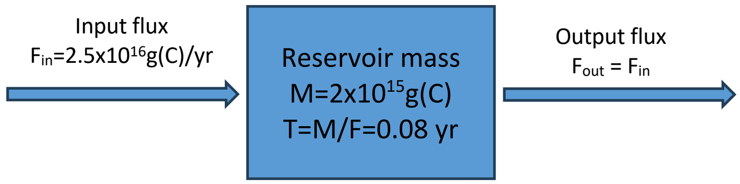
Example problems:
Example 3:
What is the residence time of carbon in living terrestrial vegetation? In marine vegetation?

1. Take a best guess.
2. Define the system (plants, e.g., trees; phytoplankton/algae)
3. Define the inflows (net primary productivity = net uptake of C by plants via photosynthesis) and outflows (death)
4. Assign numbers to the reservoirs and fluxes (assuming steady state)
   a. NPP (terrestrial) = 5×10^{16} g C y^{-1}
   b. NPP (marine) = 2.5×10^{16} g C y^{-1}
   c. M (terrestrial) = 5.6×10^{17} g C
   d. M (marine) = 2×10^{15} g C
5. Calculate a residence time ($\tau = M_i/F_{i,in}$)
   a. τ (terrestrial) = (5.6×10^{17} g C) / (5×10^{16} g C y^{-1}) = 11.2 y

b. τ (marine) = $(2 \times 10^{15}$ g C) / $(2.5 \times 10^{16}$ g C $y^{-1}) = 0.08$ y



Terrestrial biomass



Marine biomass

Example 4:

A stable and highly soluble pollutant is dumped into a lake at the rate of 0.16 tonnes per day. The lake volume is 4×10^7 m^3 and the average water flow through the lake is 8×10^4 m^3/d. Ignore evapotranspiration (i.e., the volume of the lake does not change) and assume the pollutant is uniformly mixed in the lake. Assuming the lake is at steady-state with respect to water, what eventual steady-state concentration will the pollutant reach?

1. Define the system and fluxes for both water and the pollutant
2. What is the steady-state equation for the amount of pollutant in the lake?
    a. If τ = Mass/Flux, then Mass = Flux $\times$ τ
    b. Do you have F? Yes, F = 0.16 tonnes/day. Do you have τ?
3. What is the residence time of water in the lake?
    a. = $(4 \times 10^7$ $m^3)$ / $(8 \times 10^4$ m^3/d) = 500 days
4. At steady-state, M = 0.16 tonnes/d $\times$ 500 days = 80 tonnes of pollutant in the lake
    a. Concentration = 80 tonnes / 4×10^7 m^3 = 2×10^{-6} tonnes/m^3
    b. Can be converted to more standard units, e.g., parts per million, molarity, etc.