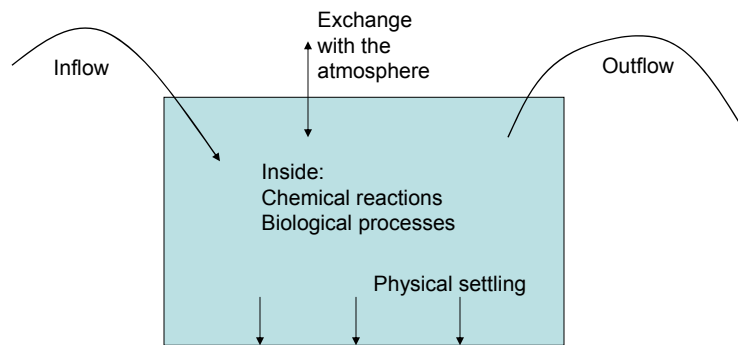


Material Balance

(Mihelcic & Zimmerman, Section 4.1; Miles & Lackey, here and there in Chapter 6)

In the environment, we are not dealing only with local processes, such as chemical reactions; we are mostly dealing with interconnected systems, implying that any sub-system is connected to other sub-systems through fluxes in and out.

We must therefore reckon with material balances in the presence of open systems.



Rules for defining a sub-system, called a "control volume".

Step 1: Choose a control volume.
This is an art rather than a science.

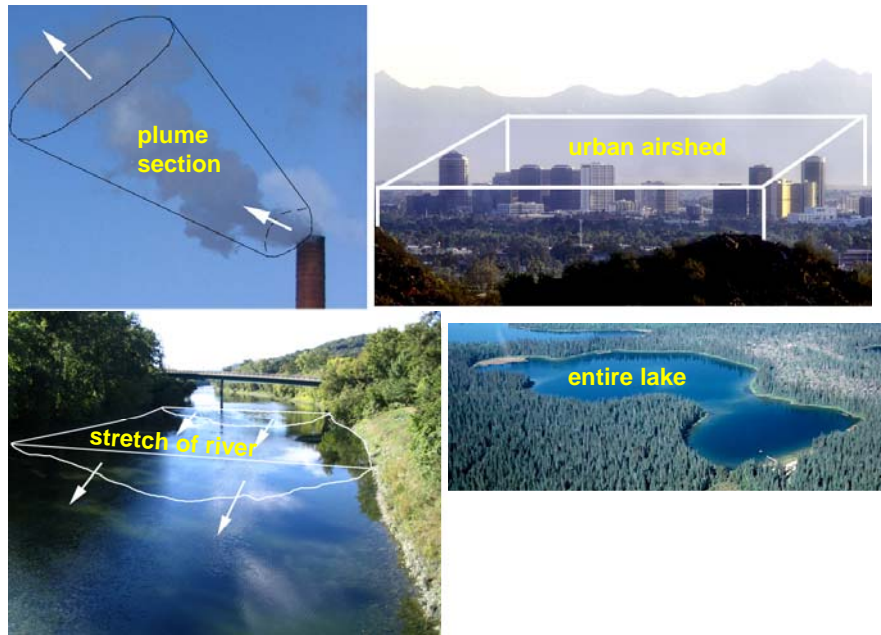
Rule 1: Boundaries must be defined clearly; you need to know whether something is inside or outside.

Rule 2: Budget must yield practical information.

Step 2: Select the substance for which the budget is to be made.
Rule: Be specific (For example: S or SO₂?)

Step 3: Consider all imports and exports.
Add sources, subtract sinks.

Examples of practical control volumes



Distinction

(Mihelcic & Zimmerman, Section 4.1.3; Mines & Lackey, Section 6.4)

Completely Mixed Flow Reactors (CMFRs)

are control volumes for which spatially uniform properties may be assumed.

Examples: Small pond, urban airshed

Plug-Flow Reactors (PFRs)

are systems along which properties vary.

They need to be split into a series of sequential control volumes.

Examples: Smokestack plume, river, estuary

Analysis on next slide applies only to CMFRs or to a single section of a PFR.

Mass balance for a CMFR

$$\text{Accumulation} = \Sigma \text{ imports} - \Sigma \text{ exports} + \Sigma \text{ sources} - \Sigma \text{ sinks}$$

$$\begin{aligned} \text{Accumulation} &= \frac{\text{amount at } (t + dt) - \text{amount at } (t)}{\text{duration } dt} \\ &= \frac{V C(t + dt) - V C(t)}{dt} = \frac{d(V C)}{dt} = V \frac{dC}{dt} \end{aligned}$$

$$\Sigma \text{ imports} = \sum_{\text{inlets}} \frac{\text{mass}}{\text{volume}} \times \frac{\text{volume of carrying fluid}}{\text{time}} = \sum_{\text{inlets}} C_{in} Q_{in}$$

$$\Sigma \text{ exports} = \sum_{\text{outlets}} \frac{\text{mass}}{\text{volume}} \times \frac{\text{volume of carrying fluid}}{\text{time}} = \sum_{\text{outlets}} C_{out} Q_{out}$$

$$\Sigma \text{ sources} = S \quad (\text{to be specified according to application})$$

$$\begin{aligned} \Sigma \text{ sinks} &= (\text{Decay constant}) \times (\text{Amount present}) \\ &= K V C \end{aligned}$$

$$\Rightarrow V \frac{dC}{dt} = \sum_{\text{inlets}} C_{in} Q_{in} - \sum_{\text{outlets}} C_{out} Q_{out} + S - K V C$$

where V = volume of control volume (in L)
 C = concentration of substance (in g/L)
 Q = volumetric flux of fluid (in L/s)
 S = sum of emissions (in g/s)
 K = decay constant (in 1/s)



Particular cases

1. *Steady state*: Concentration remaining unchanged over time

$$\frac{dC}{dt} = 0 \rightarrow \sum_{\text{inlets}} C_{in} Q_{in} - C \sum_{\text{outlets}} Q_{out} + S - K V C = 0 \rightarrow C = \frac{\sum_{\text{inlets}} C_{in} Q_{in} + S}{\sum_{\text{outlets}} Q_{out} + K V}$$

2. *Conservative substance*: No source ($S = 0$) and no decay ($K = 0$)

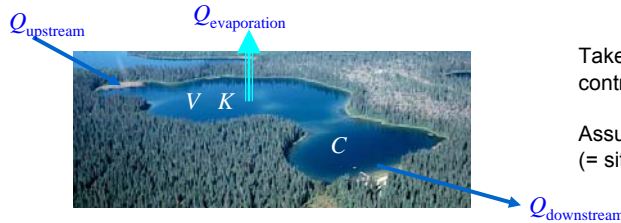
$$V \frac{dC}{dt} = \sum_{\text{inlets}} C_{in} Q_{in} - \left(\sum_{\text{outlets}} Q_{out} \right) C$$

3. *Isolated system*: No import and no export (all Q 's = 0)

$$V \frac{dC}{dt} = S - K V C \rightarrow C(t) = \frac{S}{K V} + \left(C_{\text{initial}} - \frac{S}{K V} \right) e^{-K t} \quad (\text{if } S \text{ is constant over time})$$

Example of Material Balance

A lake contains $V = 2 \times 10^5 \text{ m}^3$ of water and is fed by a river discharging $Q_{\text{upstream}} = 9 \times 10^4 \text{ m}^3/\text{year}$. Evaporation across the surface takes away $Q_{\text{evaporation}} = 1 \times 10^4 \text{ m}^3/\text{year}$, so that only $Q_{\text{downstream}} = 8 \times 10^4 \text{ m}^3/\text{year}$ exits the lake in the downstream stretch of the river. The upstream river is polluted, with concentration $C = 6.0 \text{ mg/L}$. Inside the lake, this pollutant decays with rate $K = 0.12/\text{year}$.



Take volume V of lake as the control volume.

Assume steady state
(= situation unchanging over time)

Budget is:
$$V \frac{dC}{dt} = Q_{\text{up}} C_{\text{up}} - Q_{\text{evap}} C_{\text{evap}} - Q_{\text{down}} C_{\text{down}} - KVC \quad (C_{\text{down}} = C)$$

Budget reduces to:
$$0 = Q_{\text{up}} C_{\text{up}} - (Q_{\text{down}} + KV) C$$

Solution is:
$$C = \frac{Q_{\text{up}} C_{\text{up}}}{Q_{\text{down}} + KV} = \frac{(9 \times 10^4 \text{ m}^3/\text{yr})(6.0 \text{ mg/L})}{(8 \times 10^4 \text{ m}^3/\text{yr}) + (0.12/\text{yr})(2 \times 10^5 \text{ m}^3)} = 5.19 \text{ mg/L}$$

Variation on the preceding example

Un-aided (natural) remediation

Suppose now that the source of pollution in the upstream river has been eliminated. The entering concentration in the lake has thus fallen to zero. Slowly, the concentration of the pollutant decays in the lake because of its chemical decay (K term) and flushing (Q term).

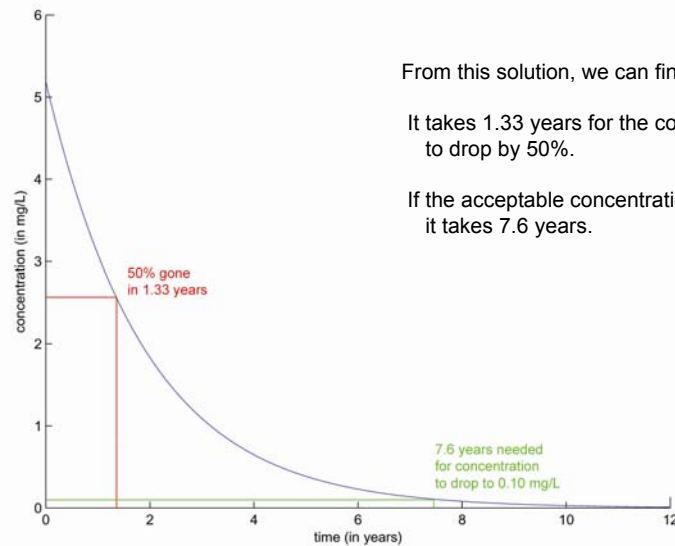
The equation becomes:

$$V \frac{dC}{dt} = Q_{\text{up}} C_{\text{up}} - Q_{\text{evap}} C_{\text{evap}} - Q_{\text{down}} C_{\text{down}} - KVC$$

$$\frac{dC}{dt} = - \left(\frac{Q_{\text{down}}}{V} + K \right) C$$

The solution to this equation is:

$$C(t) = C_{\text{initial}} \exp \left[- \left(\frac{Q_{\text{down}}}{V} + K \right) t \right] = (5.19 \text{ mg/L}) \exp(-0.52 t)$$



Question: If 7.6 years is too long, what can be done?

Check time scales of the problem:

- Residency time = $V/Q = (2 \times 10^5 \text{ m}^3)/(8 \times 10^4 \text{ m}^3/\text{yr}) = 2.50 \text{ years}$
- Decay time = $1/K = 1 / (0.12/\text{yr}) = 8.33 \text{ years}$

Conclusion: Decay is slow and flushing comparatively fast. Flushing is primarily responsible for the natural cleaning of the lake.

Adding a chemical to speed up decay would only bring incremental change, while increasing the flushing rate would have greater impact.

Mass balance for a PFR

(Mihelcic & Zimmerman, Section 4.1.5)

Most often when the Plug-Flow Reactor model is used, the actual system under consideration (river, scrubber, electrostatic precipitator) exhibits no perceptible variation over time and contains no internal sources. The only thing that is happening is a transformation along the way of the substance being traced.



The formulation below holds in the case of a gradual removal of the substance, modeled as a first-order reaction.

The material budget is most easily established if one takes the control volume as a little piece dV of the moving material (thus containing $C dV$ amount of the substance). Following this little piece of material, there is no addition or removal from it; it is a mini closed system, with the balance for the embedded substance reducing to:

$$\cancel{dV} \frac{dC}{dt} = -K(\cancel{dV})C \quad \text{The solution to this equation is: } C(t) = C(0) e^{-Kt}$$

Connecting the end concentration $C_{out} = C(t=\theta)$ to the entrance concentration $C_{in} = C(t=0)$, we write:

$$C_{out} = C_{in} e^{-K\theta} \quad \text{in which } \theta = V/Q \text{ is the total transit time through the system also the residence time in the system.}$$

Comparison between CMFR and PFR

(Mihelcic & Zimmerman, pages 122-125)

At equal system volume V and throughflow Q , the plug-flow reactor (PFR) is more efficient than the completely mixed flow reactor (CMFR). Indeed:

CMFR

$$QC_{in} = QC_{out} - KV C \Rightarrow \frac{C_{out}}{C_{in}} = \frac{1}{1 + K\theta}$$

PFR

$$C_{out} = C_{in} e^{-K\theta} \Rightarrow \frac{C_{out}}{C_{in}} = e^{-K\theta}$$

} either way with $\theta = \frac{V}{Q}$

So, why don't we always use PFRs instead of CMFRs?

