Environmental Transport and Fate

Chapter 1

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Mass & Energy Balances

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To extract useful quantitative information from a system, it is necessary
to apply the laws of physics. The most important physical laws (for our
purpose here) are:

Conservation of mass → mass of carrying fluid (air or water)
→ mass of carried contaminant (*ex*. Mercury)
→ mass of a relevant quantity (*ex*. dissolved oxygen)

Conservation of energy → total energy (mechanical + thermal)
→ usually thermal energy dominates

Finite-volume budget methodology

Step 1: Choose a control volume
This can be the entire system or only a well-chosen piece of it.

Step 2: Select the quantity for which the budget is to be made
This can be mass of fluid or the mass of a contaminant.
Be specific (For example: S or SO_2?)

Step 3: Consider all contributions, positive and negative
Add imports and subtract exports through boundaries.
Add sources and subtract sinks within the control volume.

Examples of control volumes

Cone around a smokestack plume
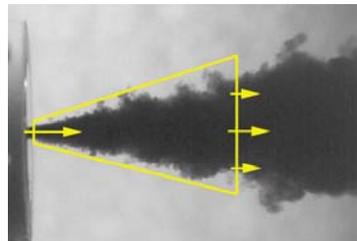
Section of a discharge jet

Section of a river

An entire lake

Phoenix, Arizona

Sometimes it is difficult to know where to place the boundaries of the control volume…

In the case of an airshed: How high should the control volume be? The general rule is: up to the top of the so-called atmospheric boundary layer. More on that later…

The choice of a control volume is more an art than a science, for there are countless possibilities.
A good level of intuition is required, which can only be developed with practice.

Notwithstanding this, there are a couple of basic rules that apply:

1. A control volume ought to be **practical**, in the sense that it should yield budget equations with the minimum number of unknowns of the problem.

2. Its **boundaries** need to be clearly defined so that there is no ambiguity about what is inside and what is outside and where are the fluxes in and out of the domain.

Let's do a budget for a generic quantity, c.

Think of it as the concentration of a contaminant:

$$c = \frac{\text{mass of substance}}{\text{volume of carrying fluid}} = \frac{m}{V} \quad \rightarrow \quad m = V c$$

In words, the budget is:

$$\text{Accumulation} \quad = \Sigma \text{ imports} \quad - \quad \Sigma \text{ exports}$$

$$+ \Sigma \text{ sources} \quad - \quad \Sigma \text{ sinks}$$

What is added $\qquad$ What is removed

$$\text{Accumulation} = \frac{\text{amount at } (t+dt) - \text{amount at } (t)}{\text{duration } dt}$$

$$= \frac{V c(t+dt) - V c(t)}{dt} = V \frac{dc}{dt}$$

$$\sum \text{imports} = \sum_{\text{inlets}} \frac{\text{mass}}{\text{volume}} \times \frac{\text{volume of carrying fluid}}{\text{area} \times \text{time}} \times \text{area} = \sum_{\text{inlets}} c_{in} \, Q_{in}$$

$$\sum \text{exports} = \sum_{\text{outlets}} \frac{\text{mass}}{\text{volume}} \times \frac{\text{volume of carrying fluid}}{\text{area} \times \text{time}} \times \text{area} = \sum_{\text{outlets}} c_{out} \, Q_{out}$$

$$\sum \text{sources} = \text{to be specified according to application} = S$$

$$\sum \text{sinks} = (\text{Decay constant}) \times (\text{Amount present}) = K V c$$

$$\Rightarrow \boxed{V \frac{dc}{dt} = \sum_{\text{inlets}} c_{in} \, Q_{in} - \sum_{\text{outlets}} c_{out} \, Q_{out} + S - K V c}$$

where
V = volume of control volume (in m^3)
c = concentration of substance (in kg/m^3)
$Q = uA$ = volumetric flux of fluid (in m^3/s)
S = sum of emissions (in kg/s)
K = decay constant (in 1/s)

Particular cases

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

$$\frac{dc}{dt} = 0 \;\rightarrow\; \sum_{\text{inlets}} c_{in}\,Q_{in} - c\sum_{\text{outlets}} Q_{out} + S - KVc = 0 \;\rightarrow\; c = \frac{\displaystyle\sum_{\text{inlets}} c_{in}\,Q_{in} + S}{\displaystyle\sum_{\text{outlets}} Q_{out} + KV}$$

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)

$$V\frac{dc}{dt} = S - KVc \;\rightarrow\; c(t) = \frac{S}{KV} + \left(c_{\text{initial}} - \frac{S}{KV}\right)e^{-Kt} \quad \text{(if } S \text{ is constant over time)}$$

Mass conservation

To state mass conservation, we use $\quad c = \dfrac{\text{mass}}{\text{volume}} = \text{density} = \rho$

And we state that there is no source and no sink.

The budget becomes: $\quad V\dfrac{d\rho}{dt} = \sum_{\text{inlets}} \rho_{\text{in}}\,Q_{\text{in}} - \sum_{\text{outlets}} \rho_{\text{out}}\,Q_{\text{out}}$

Air and water in the environmental systems behave as incompressible fluids. Thus,

$$\rho = \rho_{\text{in}} = \rho_{\text{out}} = \text{constant}$$

And the mass budget reduces to a volume budget:

$$\sum_{\text{inlets}} Q_{\text{in}} = \sum_{\text{outlets}} Q_{\text{out}} \qquad\qquad \text{Naturally !}$$

Example of Material Balance

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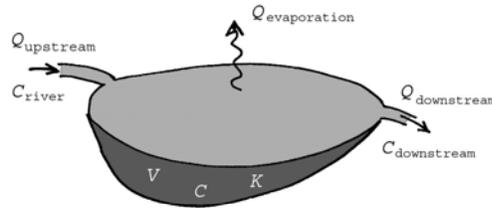
Take volume V of lake as the control volume.

Assume steady state
(= situation unchanging over time)

Budget is:
$$V\frac{dc}{dt} = Q_{up}c_{up} - Q_{evap}c_{evap} - Q_{down}c_{down} - KVc \qquad (c_{down} = c)$$

Budget reduces to:
$$0 = Q_{up}c_{up} - (Q_{down} + KV)\,c$$

Solution is:
$$c = \frac{Q_{up}c_{up}}{Q_{down} + KV} = \frac{(9\times10^4\,\mathrm{m^3/yr})(6.0\,\mathrm{mg/L})}{(8\times10^4\,\mathrm{m^3/yr}) + (0.12/\mathrm{yr})(2\times10^5\,\mathrm{m^3})} = 5.19\,\mathrm{mg/L}$$

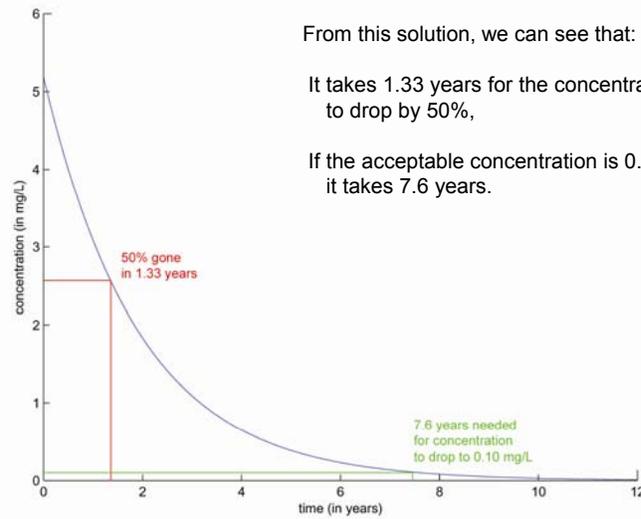### **Variation on the preceding example**   Un-aided (natural) remediation

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:

$$V\frac{dc}{dt} = Q_{up}c_{up} - Q_{evap}c_{evap} - Q_{down}c_{down} - KVc$$

$$\frac{dc}{dt} = -\left(\frac{Q_{down}}{V} + K\right)c$$

The solution to this equation is:

$$c(t) = c_{initial}\exp\left[-\left(\frac{Q_{down}}{V} + K\right)t\right] = (5.19\,\mathrm{mg/L})\,e^{-0.52t}$$

From this solution, we can see that:

It takes 1.33 years for the concentration to drop by 50%,

If the acceptable concentration is 0.10 mg/L, it takes 7.6 years.

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 years

Decay time = $1/K$ = $1/(0.12/\text{yr})$ = 8.33 years

Conclusion: Decay is slow, 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.

Another example: The smoking room at the airport (adapted from Masters, 1997)
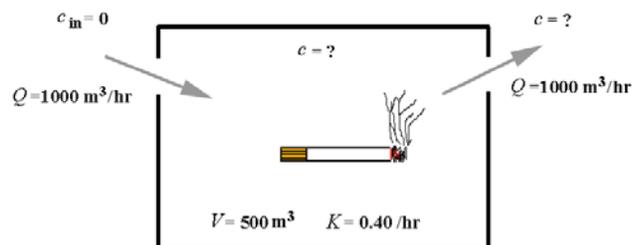
A smoking room with an air volume of 500 m³ is ventilated at the rate of 1000 m³/hr. When it opens at 7 o'clock in the morning, its air is pure and 50 smokers enter, each starting to smoke two cigarettes per hour. An individual cigarette emits, among other things, about 1.40 mg of formaldehyde, a toxin that converts to carbon dioxide at the rate of 0.40/hr.

Estimate the formaldehyde concentration at 8 and 9 o'clock, and the steady state.

If the threshold for eye irritation is 0.06 mg/m³, at what time does the smoke begin to irritate the occupants' eyes?

We solve this problem by determining first the source of formaldehyde:

$$S = 1.4 \frac{\text{mg}}{\text{cigarette}} \times 2 \frac{\text{cigarettes}}{\text{smoker} \times \text{hour}} \times 50 \,\text{smokers} = 140 \frac{\text{mg}}{\text{hour}}$$

Since the entering air is presumably fresh, $c_{in} = 0$, and there is no import.

The exiting concentration is the same as in the bar: $c_{out} = c$, and the export is Qc, where Q = 1000 m³/hr is the ventilation rate, and c the unknown indoor concentration.

The formaldehyde budget then takes the form:

$$V \frac{dc}{dt} = -(Q + KV)\, c + S$$

Taking $t = 0$ as 7am and the initial concentration $c(t=0) = 0$, fresh air when the room opens, the solution is

$$c(t) = \frac{S}{Q + KV} \left\{ 1 - \exp\left[-\left(\frac{Q}{V} + K \right) t \right] \right\}$$

With numerical values, this solution is

$$c(t) = (0.117 \text{mg/m}^3)\left[1 - \exp(-2.40\,t)\right]$$ (with t expressed in hours)

Sample numerical values are:

at 8am (t = 1 hr): c = 0.106 mg/m^3

at 9am (t = 2 hrs): c = 0.116 mg/m^3

The ultimate concentration ($t = \infty$) is

$$c_\infty = \frac{S}{Q + KV} = 0.117 \text{ mg/m}^3$$

We note that by 9am, the air in the room is almost as smoky as it will be for the rest of the day.

To address the eye irritation problem, we first compare the threshold concentration to the ultimate concentration.

Since the threshold concentration (0.06 mg/m^3) is less than the ultimate concentration (0.117 mg/m^3), the eye irritation level will be reached at some point.

Inverting the previous solution, *i.e.* solving for time as a function of concentration, we can determine the time at which eye irritation begins:

$$t = \frac{-1}{2.40} \ln\left(1 - \frac{c}{0.117}\right)$$
$$= \frac{-1}{2.40} \ln\left(1 - \frac{0.06}{0.117}\right) = 0.301 \text{ hours}$$

That is about 18 minutes after people start smoking in the room!

It is instructive to explore what action can be taken to remediate this problem by using the framework of source – pathway – receptor.

Brainstorming on the part of students here …

Heat as a pollutant → Need to consider energy conservation

In the atmosphere and surface water, there are various forms of energy:
- kinetic (due to motion),
- potential (due to elevation), and
- thermal (due to heat content).

Almost always, the thermal energy dwarfs the other three.

For example: Heating 1 kg of water by 1°C takes 4184 J
                Heating 1 kg of air by 1°C takes 1005 J (at constant pressure)
                1 kg of air or water moving at 10 m/s has 50 J of kinetic energy
                1 kg of air or water falling down 50 m releases 490 J of potential energy

The result is that the energy budget reduces in good first approximation to a
heat budget:

Accumulation of heat = Heat entering – Heat exiting
+ Heat sources – Heat sinks

Furthermore, sources and sinks are rarely internal but occur most often at
boundaries. Thus,

Accumulation of heat = Heat entering – Heat exiting

Heat content = Thermal energy = Internal energy

m = mass of substance
C_v = heat capacity of substance
T = temperature of substance
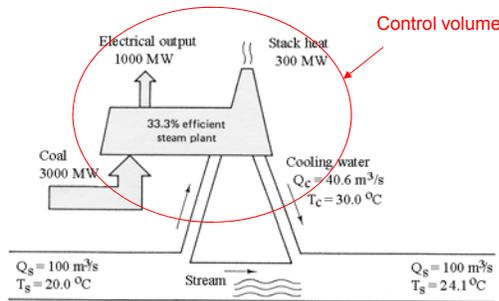ρ = density of substance

$$= m\, C_v\, T$$

Per unit volume: $\rho\, C_v\, T$

Budget:

$$V \frac{d}{dt}(\rho\, C_v\, T) = \sum_{\text{inlets}} (\rho\, C_v\, T_{\text{in}})(u_{\text{in}}\, A_{\text{in}}) - \sum_{\text{outlets}} (\rho\, C_v\, T_{\text{out}})(u_{\text{out}}\, A_{\text{out}})$$

$$V \frac{dT}{dt} = \sum_{\text{inlets}} T_{\text{in}}\, Q_{\text{in}} - \sum_{\text{outlets}} T_{\text{out}}\, Q_{\text{out}}$$

Example of heat as a pollutant

$$P_{\text{electricity}} = 1000 \ \text{MW}$$

$$P_{\text{total}} = \frac{1000 \ \text{MW}}{0.333} = 3000 \ \text{MW}$$

$$P_{\text{waste heat}} = 3000 \ \text{MW} - 1000 \ \text{MW}$$
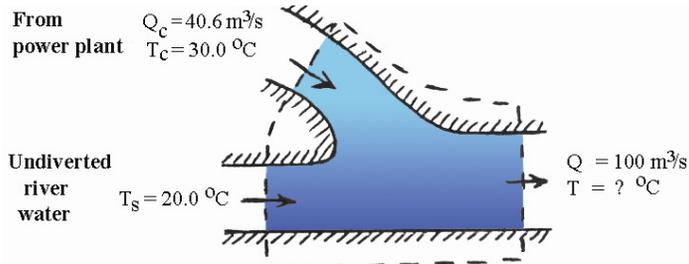$$= 2000 \ \text{MW}$$

$$P_{\text{to river}} = 2000 \ \text{MW} - 300 \ \text{MW}$$
$$= 1700 \ \text{MW}$$

Heat budget:

Exiting heat = Entering heat + Heat delivered to water

$$\rho \, C_v \, T_{\text{exiting}} \, Q_c = \rho \, C_v \, T_{\text{entering}} \, Q_c + 1700 \ \text{MW}$$

$$Q_c = \frac{1700 \ \text{MW}}{\rho \, C_v \, (T_{\text{exiting}} - T_{\text{entering}})} = \frac{1700 \times 10^6 \ \text{J/s}}{(1000)(4184)(30 - 20)} = 40.63 \ \text{m}^3/\text{s}$$

$$0 = Q_{\text{upstream}} \, T_{\text{upstream}} + Q_{\text{diverted}} \, T_{\text{diverted}} - Q_{\text{downstream}} \, T_{\text{downstream}}$$

Solve for $T_{\text{downstream}}$:

$$T_{\text{downstream}} = \frac{(40.63 \times 30) + (59.37 \times 20)}{100} = 24^\circ\text{C}$$

The power plant increases the river temperature by 4 degrees Celsius.

If this is excessive, what can be done?