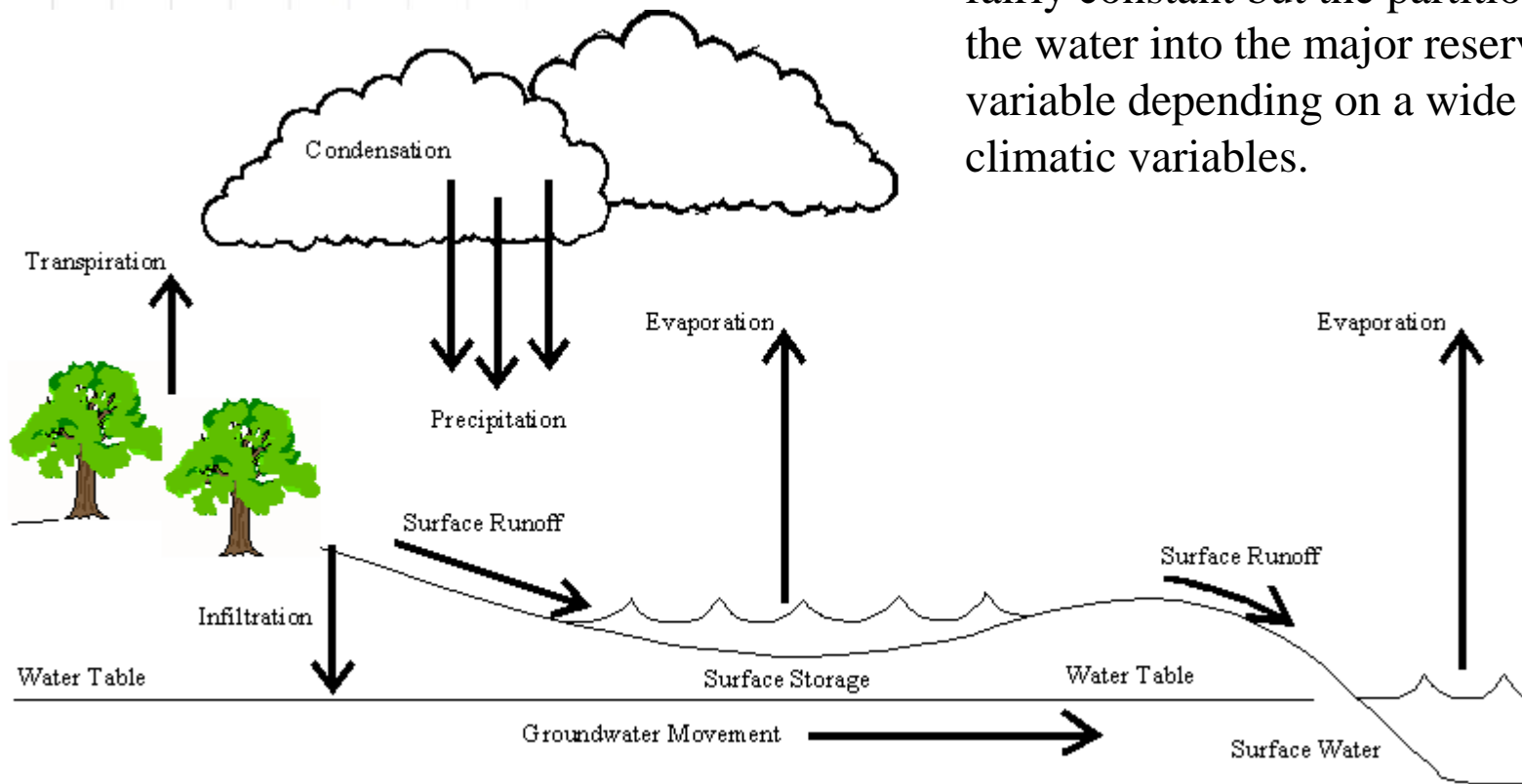# BAE 820 Physical Principles of Environmental Systems

Fate and transport of pollutants in the water environment

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The global hydrologic cycle

The mass of water on Earth remains fairly constant but the partitioning of the water into the major reservoirs is variable depending on a wide range of climatic variables.

Water table aquifer

- Part of precipitation that falls on soil may infiltrate and replenish soil moisture. Water that drains downward may finally reach a level at which all of the voids in the earth's materials are filled with water (zone of saturation).

- A water table describes the boundary between water-saturated ground and unsaturated ground. Below the water table, rocks and soil are full of water. Pockets of water existing below the water table are called aquifers.

- Water table is influenced by many factors, including topography, geology, weather, ground cover, and land use, and it usually isn't flat, or horizontal. It is generally 15 to 90 meters (50 to 300 feet) below the land surface.
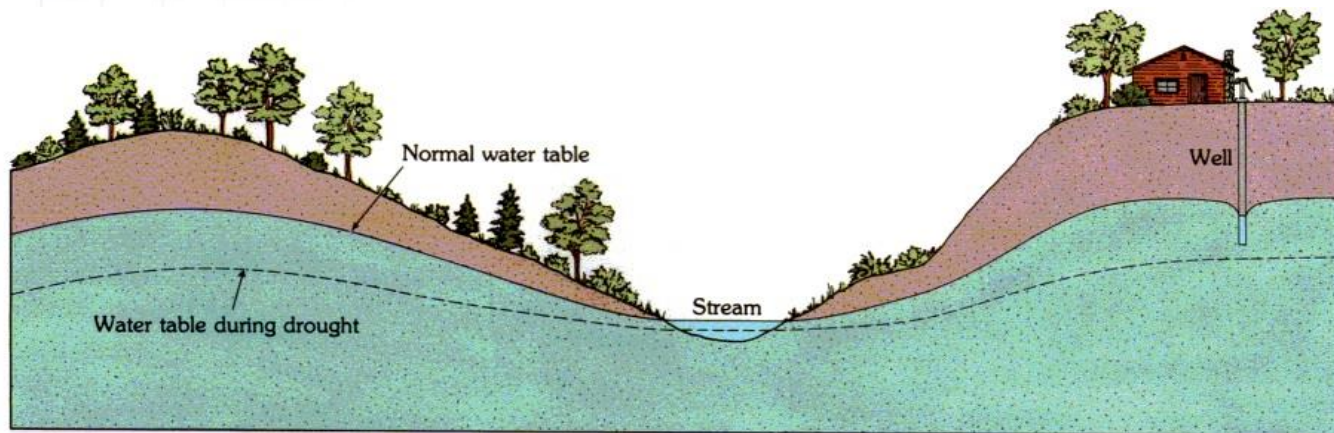
The hydrological equation

The global system is considered to be a closed system and is in mass balance. Assuming the density of water is constant throughout the system, we have

$$V_P - V_S - V_R - V_G - V_E - V_T = 0$$

Where

- V_P is volume of precipitation
- V_S is volume of storage
- V_R is volume of runoff
- V_G is volume of groundwater infiltration
- V_E is volume of evaporation
- V_T is volume of transpiration.

- In contrast to the global system, most of the problems we are interested in are open systems. We can modify the basic hydrologic equation by considering hydrologic subsystem as a mass balance problem.

Rate of accumulation = rate of input – rate of output

Runoff analysis

Estimating runoff through rational method is one of the simplest application of the hydrologic equation. The only input is precipitation, and the only output is direct runoff. At steady state the storage term is zero. Since few natural surface are completely impervious, we can account for this loss using runoff coefficients (the fraction of rainfall that becomes runoff, which is a function of the soil type and drainage basin slope).

$$Q=CiA$$

Where,

- Q is peak runoff rate;
- C is runoff coefficient;
- i is rainfall intensity;
- A is area of watershed.

Ground cover	Runoff coefficient	Ground cover	Runoff coefficient
Lawns	0.05-0.35	Pasture	0.12-0.62
Residential areas	0.3-0.75	Forest	0.05-0.25
Pavement	0.70-0.95	Cultivated land	0.08-0.41
Roofs	0.75-0.95	Unimproved areas	0.1-0.3

Evaporation analysis

The loss of water from surface water is a function of solar radiation, air and water temperature, wind speed, and the difference in vapor pressures at the water surface and in the overlying air. One of empirical equations for estimating evaporation is

$$E = 1.22 \, (e_s - e_a)u$$

Where,

- E is evaporation rate, mm/d;
- e_s is saturation vapor pressure, kPa;
- e_a is vapor pressure in the overlying air, kPa;
- u is wind speed, m/s.

Temperature, ºC	Water vapor pressure, kPa	Temperature, ºC	Water vapor pressure, kPa
0	0.611	25	3.167
5	0.872	30	4.243
10	1.227	35	5.642
15	1.704	40	7.378
20	2.337	50	12.34

Example

- The wind speed over a lake is 4.0 m/s. The air temperature averaged 20ºC and the relative humidity is 30%. The water temperature averaged 10ºC. Estimate the evaporation rate.

- Solution: The air temperature averaged 20ºC, so

$$e_a = 2.337 \times 30\% = 0.70 \text{kPa}$$

The water temperature averaged 10ºC, so

$$e_s = 1.227 \text{ kPa}$$

Therefore,

$$E = 1.22 (e_s - e_a)u = 1.22 (1.227 - 0.70) \times 4.0 = 2.57 \text{ mm/d}$$

Source of water pollution

- Water pollution sources are categorized as point source and nonpoint source.
  - Point sources mainly include industrial wastes and domestic sewage because they are generally collected by a network of pipes or channels and conveyed to a single point of discharge into the watercourses.
  - Nonpoint sources are characterized by multiple discharge points and mainly include urban and agricultural runoff.

- Major pollutant categories
  - Oxygen demanding material
  - Nutrients
  - Pathogenic organisms
  - Suspended solids
  - Salts
  - Toxic metals and toxic organic compounds
  - Heat

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Aerobic and anaerobic decomposition

•   Organic materials enter watercourses at high energy level. Decomposition or biodegradation of them may take place using free oxygen or in the absence of free oxygen. Aerobic and anaerobic decomposition are usually performed by a completely different set of microorganisms.

–   The basic equation for aerobic decomposition is

$$HCHO + O_2 \rightarrow CO_2 + H_2O + energy$$

–   The basic equation for anaerobic decomposition is

$$2HCOH \rightarrow CH_4 + CO_2 + energy$$

•   One of the most serious effects of water pollutants is depletion of dissolved oxygen. All higher forms of aquatic life exist only in the presence of oxygen, and most desirable microbiologic life also requires oxygen. Natural streams and lakes are usually aerobic. If a watercourse becomes anaerobic, the ecology changes and the water becomes unpleasant and unsafe.

Biochemical oxygen demand in water

- Biochemical oxygen demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. It is widely used as an indication of water quality. It is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20 °C and is noted as BOD_5.

- BOD is similar in function to chemical oxygen demand (COD), in that both measure the amount of organic compounds in water. COD measures everything that can be chemically oxidized, rather than just levels of biologically active organic matter.

- The BOD curve:

$$BOD(t) = L_0(1-e^{-kt})$$

- It may also be written in base 10:

$$BOD(t) = L_0(1-10^{-Kt})$$

Where L_0 is the ultimate oxygen demand. It is oxygen equivalent of organics at time=0. The two rate constants are related as in k=2.303K.

Example

- If the BOD_3 of a waste is 75 mg/L, and the K is 0.150 day^{-1}, what is the ultimate BOD?

- Solution: Note the rate constant is given in base 10 (K vs k), we have

$$75 = L_0(1-10^{-Kt}) = L_0(1-10^{-0.150\times3}) = 0.645L_0$$
$$L_0 = 75/0.645 = 116 \text{ mg/L}$$

Or,

$$k=2.303K=0.345$$
$$75 = L_0(1-e^{-kt}) = L_0(1-e^{-0.345\times3}) = 0.645L_0$$
$$L_0 = 75/0.645 = 116 \text{ mg/L}$$

Typical values for the BOD rate constant at 20ºC

Sample	K (day^{-1})	k (day^{-1})
Raw sewage	0.15-0.30	0.35-0.70
Well-treated sewage	0.05-0.10	0.12-0.23
Polluted river water	0.05-0.10	0.12-0.23

DO sag curve in rivers (Streeter–Phelps equation)

The concentration of dissolved oxygen (DO) in a river is an indicator of the general health of the river. All rivers have some capacity for self-purification. The capability of a river to absorb a waste load can be assessed by determining the profile of DO concentration downstream from a waste discharge.

Define the oxygen deficit $D = DO_s - DO$

Where

- DO_s is saturation concentration of dissolved oxygen;
- DO is actual concentration of dissolved oxygen.

$$\frac{dD}{dt} = k_d L - k_r D$$

Where

- k_d is deoxygenation rate constant
- L is ultimate BOD of river water;
- k_r is reaeration rate constant;
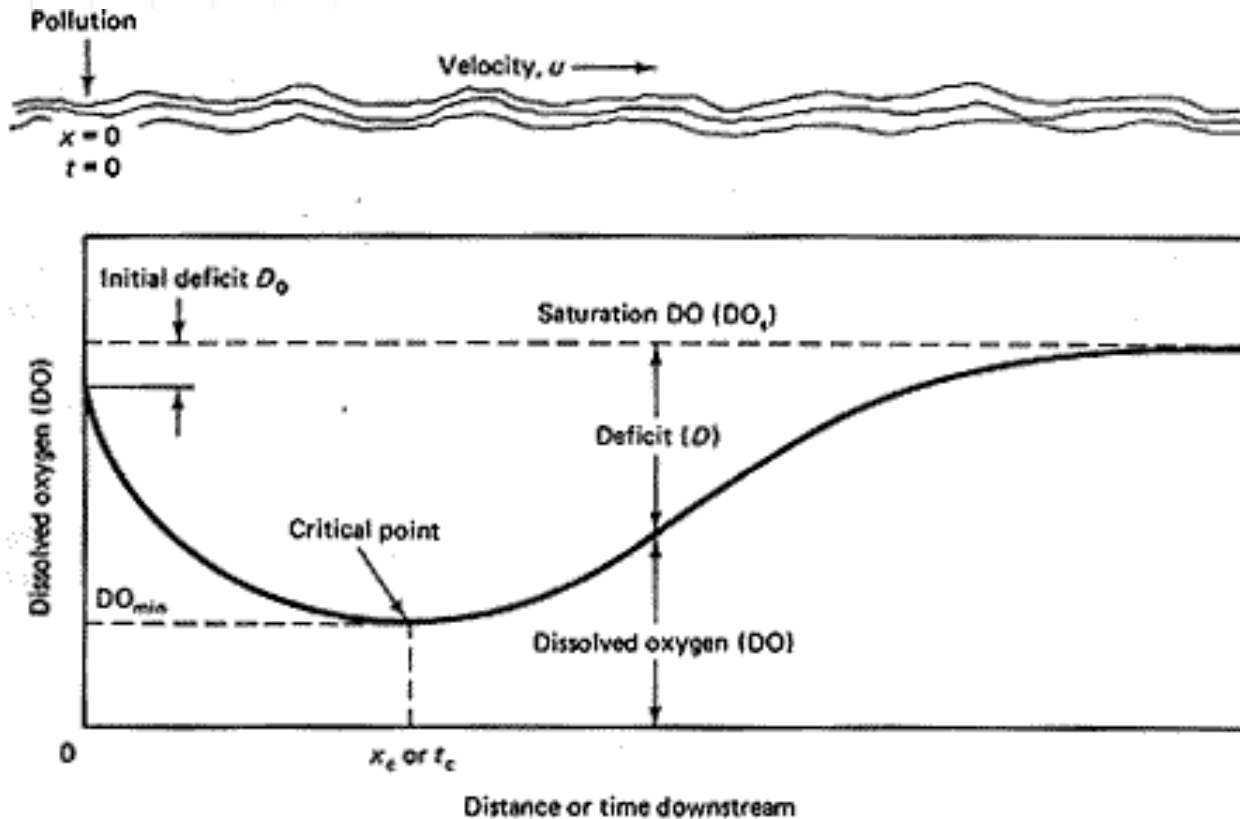- D is oxygen deficit in river water.

Solve the equation,

$$D = \frac{k_d L_0}{k_r - k_d} [\exp(-k_d t) - \exp(-k_r t)] + D_0 \exp(-k_r t)$$

DO sag curve in rivers

The lowest point on the DO sag curve is called the critical point. The time to the critical point

$$t_c = \frac{1}{k_r - k_d} ln[\frac{k_r}{k_d} (1 - D_0 \frac{k_r - k_d}{k_r L_0})]$$

Then the critical oxygen deficit can be found by using this critical time.

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Saturation values of dissolved oxygen in fresh water exposed to atmosphere containing 20.9% oxygen under a pressure of 101.325 kPa

Temperature, ºC	Dissolved oxygen, mg/L	Temperature, ºC	Dissolved oxygen, mg/L
0	14.62	15	10.15
1	14.23	16	9.95
2	13.84	17	9.74
3	13.48	18	9.54
4	13.13	19	9.35
5	12.80	20	9.17
6	12.48	21	8.99
7	12.17	22	8.83
8	11.87	23	8.68
9	11.59	24	8.53
10	11.33	25	8.38
11	11.08	26	8.22
12	10.83	27	8.07
13	10.60	28	7.92
14	10.37	29	7.77

Example

- Bald eagle river has a flow rate of 0.43 m³/s (v=0.03m/s) and ultimate BOD of 5.0 mg/L. A town discharges 0.20 m³/s of treated wastewater (ultimate BOD=26.6 mg/L) into the river. The DO of the river is 6.5 mg/L and the DO of the wastewater is 1.0 mg/L. Determine the DO concentration at a point 5km downstream from the discharge. Given T=10ºC, k_d=0.0344 d^{-1}, k_r=0.0477 d^{-1}.

- Solution:

At T=10ºC, DOs = 11.33 mg/L

The initial deficit after mixing is

$$D_0 = DOs - DO = 11.33 - \frac{0.20 \times 1.0 + 0.43 \times 6.5}{0.20 + 0.43} = 11.33 - 4.75 = 6.58 \text{mg/L}$$

The initial ultimate BOD after mixing is

$$L_0 = \frac{0.20 \times 26.6 + 0.43 \times 5.0}{0.20 + 0.43} = 11.86 \text{ mg/L}$$

The travel time

$$t = \frac{5000}{0.03 \times 24 \times 3600} = 1.929 \text{ d}$$

Example

Then the deficit can be estimated as

$$D = \frac{0.0344 \times 11.86}{0.0477 - 0.0344} [\exp(-0.0344 \times 1.929) - \exp(-0.0477 \times 1.929)] + 6.58 \exp(-0.0477 \times 1.929)$$

$$= 30.83 \times (0.9358 - 0.9122) + 6.58 \times 0.9122 = 6.73 \text{ mg/L}$$

$$DO = 11.33 - 6.73 = 4.60 \text{ mg/L}$$

The critical time

$$t_c = \frac{1}{0.0477 - 0.0344} \ln[\frac{0.0477}{0.0344} (1 - 6.58 \frac{0.0477 - 0.0344}{0.0344 \times 11.86})] = 6.45 \text{ d}$$

The critical deficit

$$D_c = \frac{0.0344 \times 11.86}{0.0477 - 0.0344} [\exp(-0.0344 \times 6.45) - \exp(-0.0477 \times 6.45)] + 6.58 \exp(-0.0477 \times 6.45)$$

$$= 6.85 \text{ mg/L}$$

The critical DO

$$DO_c = 11.33 - 6.85 = 4.48 \text{ mg/L}$$

The critical DO occurs downstream at a distance of

$$6.45 \times 24 \times 3600 \times 0.03 = 16700 m = 16.7 \ km$$

Estimation of deoxygenation rate k_d and reaeration rate k_r

- Typically, k_d may vary within the range 0.05-0.5 d^{-1} and k_r can range from 0.4 to 1.5 d^{-1}. Several estimations of the rates using characteristics of the stream exists.
- Deoxygenation rate

$$k_d = k + \frac{v}{H}\eta$$

- Reaeration rate

$$k_r = \frac{3.9 v^{0.5}}{H^{1.5}}$$

Where k is BOD rate constant determined in laboratory at 20 °C, d^{-1}; v is average speed of stream flow, m/s; H is average depth of stream, m; η is bed-activity coefficient which may vary from 0.1 for stagnant or deep water to 0.6 or more for rapidly flowing streams.

- Temperature correction: Both the deoxygenation rate k_d and reaeration rate k_r can be temperature corrected, following the general formula.

$$k = k_{20}\theta^{(T-20)}$$

Where k_{20} is the rate at 20 °C; θ is a constant, normally $\theta = 1.048$ for k_d and $\theta = 1.024$ for k_r; T is the actual temperature in the stream in °C.

Pollutants in rivers

The surface water in fast-flowing streams are generally unmixed in the direction of flow. This suggests that the axial dispersion term in the advection-dispersion equation can be neglected.

Loss of pollutants = Loss to air + Loss to sediment + Reaction loss

Therefore,

$$-\frac{dC}{dt} = K_L (C_L - \frac{C_G}{K_H})/h + K_S(C_L - \frac{C_S}{K_{Sw}})/h + k_r C_L$$

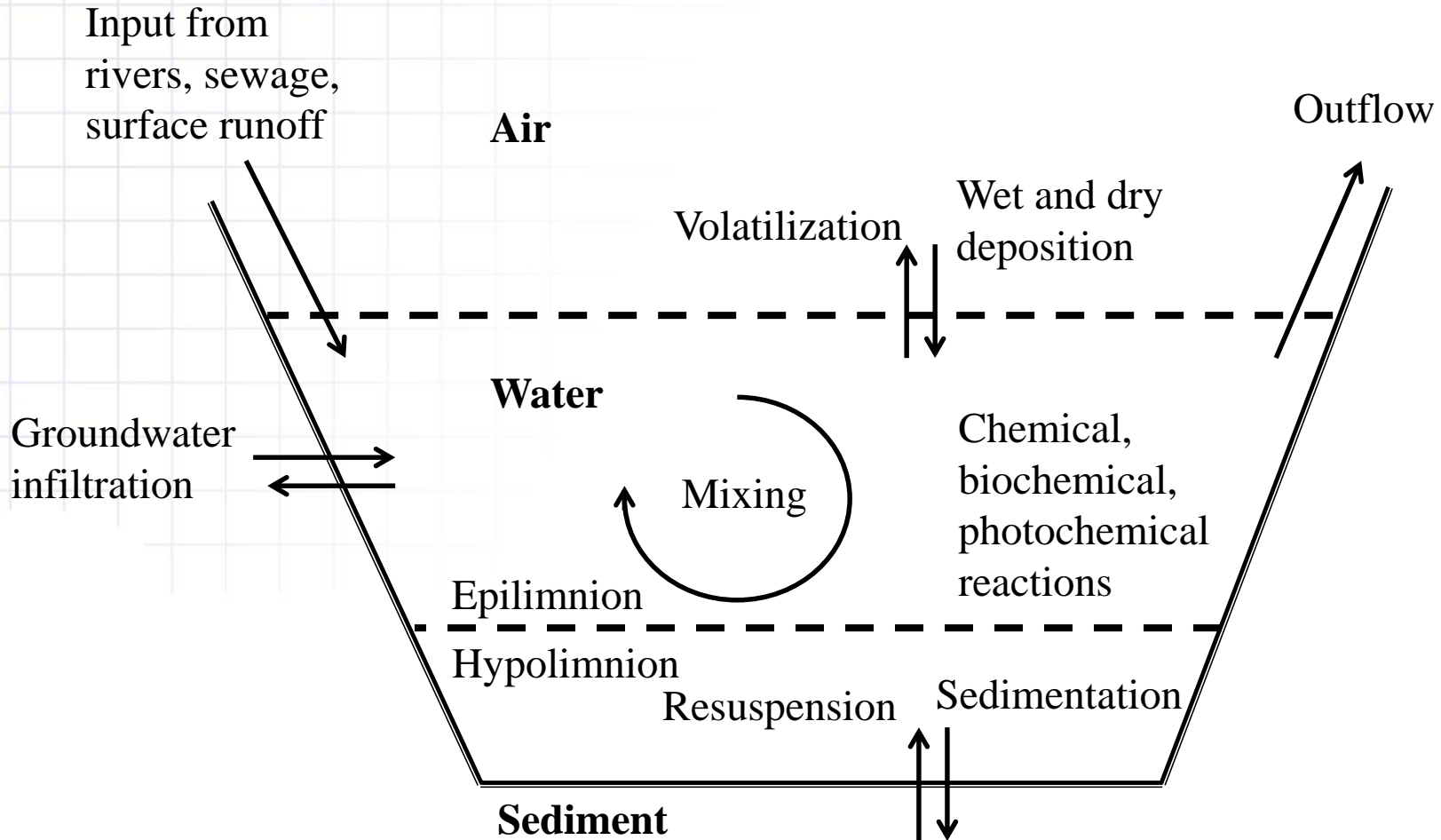$$C_L(t) = C_{L0}\exp(-\alpha t) + \frac{\beta}{\alpha}[1-\exp(-\alpha t)]$$

Where,

- α is a composite rate constant that characterizes each loss mechanism within the water, $\alpha = K_L/h + K_S/h + k_r,$

- $\beta = \frac{K_L C_G}{hK_H} + \frac{K_s C_s}{hK_{SW}}$

Example: Loss of chloroform from a shallow stream

- For an episodic spill of chloroform in the river, estimate its concentration 20 miles downstream. Depth of the river is 2m, average flow velocity is 1 m/s, $K_L = 0.14$ m/h, $k_r = 4.2 \times 10^{-8}$ h^{-1}. Due to the high stream velocity, the water-to-air mass transfer is likely to dominate over the water-to-sediment mass transfer. Assume the background concentrations of chloroform in air and sediment are negligible.

- Solution: β is negligible
  $\alpha \approx K_L / h + k_r = 0.14/2 + 4.2 \times 10^{-8} = 0.07$ h^{-1}
  $t = 20$ mile $\times 1609$ m/mile $\times 1$ m/s $\times 3600$ s/h $= 8.9$ h
  $C(t)/C_0 = \exp(-0.07/8.9) = 0.53$
  Therefore, the concentration at 20 miles downstream will be 53% of its concentration at the spill point.

Pollutants in lakes

Input from rivers, sewage, surface runoff

Air

Outflow

Volatilization

Wet and dry deposition

Water

Groundwater infiltration

Mixing

Chemical, biochemical, photochemical reactions

Epilimnion

Hypolimnion

Resuspension

Sedimentation

Sediment

A simple box model

$$\text{Accumulation} = \text{Input} - \text{Output} - \text{Reaction loss}$$

Therefore,

$$\frac{dC}{dt} = k_F(C_F - C) - (k_{voln} + k_{sed} + k_{rxn} + k_{bio} + k_{photo})C$$

Where

- C is the total concentration of compound in the epilimnion;
- k_F = feed rate/epilimnion volume is the rate constant for flushing;
- k_{voln}, k_{sed}, k_{rxn}, and k_{bio} are rate constants for volatilization, sedimentation, chemical, biochemical, and photochemical reactions. They are specific to chemicals.

Evaporation from a well-stirred surface

$$\frac{V}{A}\frac{dC_L}{dt} = z\frac{dC_L}{dt} = K_L(C_L - C_L*) = K_L(C_L - \frac{C_G}{K_H})$$

If background air concentration is negligible, $C_G \approx 0$,

$$C_L(t) = C_{L0}\exp(-\frac{K_L}{z}t) = C_{L0}\exp(-k_{voln}t)$$

The half-life for evaporation is

$$t_{1/2} = 0.693/k_{voln} = 0.693z/K_L$$

Mackay and Leinonen (1975) gives values of K_L for several compounds at 298K.

Compound	K_L (m/h)	$t_{1/2}$ (h) for z=1m
Benzene	0.144	4.8
Biphenyl	0.092	7.5
Aldrin	0.00372	186.3
Mercury	0.092	7.5

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Problem Solution #10

- NH_3 concentration is 10 mg/m^3 at T=273K, P=1.013×10^{5}Pa. What is the mixing ratio in ppm?

- C(ppm)= C(mg/m^3)×1000×8.314×T/P/M

    =10×1000×8.314×273/1.013×10^5/17

    =13 ppm