CENG 6405: Pollutant Fate and Transport

Chapter 2 Transport in Surface Water

- 1. Transport in river system
 - 1. Water velocity and stream flow regimes
 - 2. Settling and transport with sediments
 - 3. Mass-balance equations
 - 4. Non-conservative pollutants
 - 5. Self-purification and the oxygen balance
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2.1. Transport in river system

- As society becomes more industrialized the variety of waste materials increases and in many countries the problems of water quality are more demanding than water quantity.
- In order to manage a river system and maintain adequate water quality, it is essential to understand the mechanisms governing pollution and self purification processes.
- The interactions between physical, chemical and biological processes ensure that, forecasting the impact of an effluent on a river system is particularly difficult.

2.1.1 Water velocity and stream flow regimes

 Any substance present in flowing water moves with the current (advective transport). It is accomplished by:

Gravity; the forces in the curves of a river section and wind.
Erosion of the river bed in upper reaches and the transport in the middle reach and deposition at lower reach is the usual processes in a river. These 3 processes (erosion, transport and deposition) can be observed at one and the same time.

• **River bed** is considered to be relatively **stable** (some times called **rigid**) when **erosion and deposition are in balance**.

Velocity distribution in open channels



 Despite the apparent complexity of water velocities in rivers it is still possible to define an overall mean velocity for movement of pollutants in river systems.

Velocity distribution in open channels



Secondary circulation

- Because of a variety of reasons including the resistance flow due to stream banks, a rotational or cellular movement of flow will occur in the main channel. This flow component that is not in the main flow direction has been termed secondary circulation, secondary flow, secondary current, or transverse current and these currents can carry the pollutants in the transverse plane of the flow cross-section.
- At present, the knowledge of this secondary current is limited.
 However recent investigations have revealed that their effects are far greater than the turbulent diffusion processes.

Velocity distribution in natural streams

Secondary circulation in broken lines

• At low discharge

• At high discharge



2.1.2 Settling and transport with sediments

- During high flow, by the increased turbulence, natural aeration processes are enhanced.
- During low flow dilution of pollutants is reduced, sediments
 together with adsorbed pollutant settle.
- Intensive rain, following periods of low flow, creates larger velocity and scouring of settled sediments.
- In large rivers with comparatively shallow water and low water velocities the natural mixing processes are reduced and nonhomogeneity of the chemical composition of water is observed.

Transport with sediment

- If the pollutant contains particulate matter or if it coats the sediment particles present in the alluvial streams as a result of adsorption, then the transport of the pollutant are governed by the mechanisms controlling the motion of the sediment particles.
- The strength of the flow needed to initiate the motion of the sediment particles forming the bed can be predicted using the well-known **Shields Curve** shown in Figure next slide.
- The grain size Reynolds Number X, expresses the balance between the inertia and friction forces and is given by:

$$\bullet X = \frac{D_{50}\rho v_*}{\mu}$$

•Where μ is the dynamic viscosity of the fluid

Shields Curve for sediment transport



Transport with sediment

• The mobility number Y expresses the balance between the shear stress (τ_0) exerted by the flow on the bed and the weight of a solid particle per unit surface area:

$$Y = \frac{\rho v_*^2}{D_{50} \gamma_s} = \frac{\tau_o}{\gamma (s-1) D_{50}} \text{ in which } v_* = \sqrt{\frac{\tau_o}{\rho}}$$

- where ρ is the density of the fluid, v_* is the shear velocity of the flow, γ_s is the submerged specific weight of the solid particle and D₅₀ is the size of the particles by mass.
- The values of Y_{cr} and X_{cr} are those resulting from the use of critical values of v_* (i.e. v_{*cr}).
- If $Y < Y_{cr}$ then the particles will not moved by the flow.

Transport with sediment

- If the strength of the flow increases, increasing the shear stress at the bottom and consequently the mobility number Y, the particles begin to move.
- If $1 \le Y/Y_c \le 15$, the particles move in the vicinity of the bed by rolling and performing short jumps. The particles advance along the bed in a series of alternate rest and transport periods.
- For values of $Y/Y_c > 15$, the sediments move in suspension like the fluid particles. Dispersion of the sediment particles during this stage of motion can be formulated in the same way as for the fluid particles.

Example 2.1

- Water flows at a depth of 0.3 m in a wide stream having slope of 0.001. The median diameter of the sand on the bed is 1.0 mm. Determine whether the contaminated grains are stationary or moving ($v = 1.007 \times 10^{-6} \text{ m}^2/\text{s}$).
- Solution:

$$\tau_o = \gamma \frac{A}{P}S = \gamma hS = 1000 \times 9.81 \times 0.3 \times 0.001 = 2.943Pa$$
$$v_* = \sqrt{ghS} = \sqrt{9.81 \times 0.3 \times 0.001} = 0.0542m/s$$
$$X_c = \frac{v_* D_{50}}{v} = \frac{0.0542 \times 0.001}{1.007 \times 10^{-6}} = 53.87$$

• from shield's diagram $for X_c = 53.87, Y_c \cong 0.04$

 $Y = \frac{\tau_o}{\gamma(s-1)D_{50}} = \frac{2.943}{1000 \times 9.81 \times (2.65 - 1) \times 0.001} = 0.182 > 0.04$ Shields diagram: Contaminated Sediment will move in the vicinity of the bed (rolling and saltating)

2.1.3 Mass-balance equations

 For a conservative substance (those substances which do not undergo any process other than dilution (the processes such as decay, chemical reactions and production or removal are not considered). The conservation of mass principle leads to the commonly used mass balance equation expressed as: (Eq. a)

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} = \frac{\partial}{\partial x} \left((D + \varepsilon_x + E_x) \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left((D + \varepsilon_y + E_y) \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left((D + \varepsilon_z + E_z) \frac{\partial C}{\partial z} \right)$$

• It is assumed that the molecular diffusion coefficient **D** is isotropic whereas the turbulent diffusion coefficient ε , and Dispersion coefficient **E** are anisotropic

Molecular diffusion (reminder)

- According to Fick's law: $F_l = -D \frac{\partial C}{\partial x}$,
- where F_l is the amount of substance diffusing per unit area per unit time; C is the concentration; x is the distance measured normal to the section and D is the diffusion coefficient.
- The minus (-) sign is due to the fact that the transfer of substance takes place in a direction along the decreasing concentration.
- The molecular diffusion process plays a significant role in laminar flows; but in the case of turbulent flows its effects are negligible in comparison to the 'turbulent diffusion process'.

Turbulent diffusion (reminder)

- The spreading of pollutants due to the random motion of the fluid 'particles' in a turbulent flow is termed turbulent diffusion.
- The amount of substance (F_t) diffusing per unit area of a section per unit time due to turbulent diffusion is expressed in terms of a (turbulent) diffusion coefficient ε and the concentration gradient

of the diffusing substance as: $F_t = -\varepsilon \frac{\partial C}{\partial x}$

 Spreading of a substance due to turbulent diffusion is much more rapid than that due to molecular diffusion. The numerical values of ε are far greater than those of D.

Dispersion of pollutants



In the tracer experiment,
illustrated in Figure AA, the
'bell shaped' nature of the curve
is an indication of the dispersive
properties of a stream.

• The dispersion process represents an important factor when assessing pollution problems.

Mass balance equation

• For the case of sediment particles which are heavier than water and which have a fall velocity of ω in the z direction, the mass balance equation can be Written as:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} + (w - \omega) \frac{\partial c}{\partial z} = \frac{\partial}{\partial x} \left((D + \varepsilon_x + E_x) \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left((D + \varepsilon_y + E_y) \frac{\partial c}{\partial y} \right) + \frac{\partial}{\partial z} \left((D + \varepsilon_z + E_z) \frac{\partial c}{\partial z} \right)$$

• For reasons indicated earlier, if the effect of the molecular diffusion is negligible in comparison to that of turbulent diffusion, then D can be left out of the above equation

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + (w - \omega) \frac{\partial C}{\partial z} = \frac{\partial}{\partial x} \left((\varepsilon_x + E_x) \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left((\varepsilon_y + E_y) \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left((\varepsilon_z + E_z) \frac{\partial C}{\partial z} \right)$$

- For C (x, y, z, t) prediction, in addition to appropriate initial & boundary conditions provision, u, v, w, D, ε_x, ε_y, ε_z, E_x, E_y, and E_z at every point in the flow field need to be known.
- Such a detailed description is usually not available for the natural streams and therefore, the mass balance equation is often simplified by making certain assumptions regarding the flow field and the diffusion processes.
- Some of the commonly made simplifications will be considered here.

Longitudinal dispersion: cross-sectional average mass-balance eq.

- Taylor (1954) described the spreading of a neutrally buoyant, conservative pollutant transport in pipes by assuming:
- The motion is predominantly in one direction, i.e. v = w = 0;
- ^{2.} The turbulent diffusion in the y and z directions of motion is negligible, i.e. $\varepsilon_y = \varepsilon_z = 0$;
- The molecular diffusion is negligible, i.e. D = 0.
- By averaging over the entire cross-section and writing

 $\bullet u = \bar{u} + u' and \ C = \bar{C} + C'$

• where the over-bar denotes averages over the cross-section and u' and C' represent spatial variations from the mean, **Eq. a** can be written as: $\frac{\partial \bar{C}}{\partial t} + \bar{u} \frac{\partial \bar{C}}{\partial x} = E \frac{\partial^2 \bar{C}}{\partial x^2}$

Which is the well-known Taylor's one-dimensional dispersion equation. E is as the longitudinal dispersion coefficient.

Taylor's equation

 In a uniform channel with constant stream velocity, the dispersion coefficient may be calculated from a tracer curve

as:
$$E = \frac{\sigma^2 \bar{u}^3}{2L}$$

- where L is the distance travelled and σ^2 is the variance of the concentration curve of the type shown in Figure AA.
- It should be pointed out that Taylor's one-dimensional approach does not apply in regions close to the location where the pollutants are injected.

Longitudinal spreading of a conservative pollutant

- Consider the longitudinal spreading of a slug of a conservative pollutant injected instantaneously in a natural stream. The transport of this slug of pollutant can be described by the cross-sectional average mass balance equation. $\frac{\partial \bar{C}}{\partial t} + \bar{u} \frac{\partial \bar{C}}{\partial x} = E \frac{\partial^2 \bar{C}}{\partial x^2}$
- The Solution of this equation can be expressed as:

$$\bar{C}(x,t) = \frac{M}{A} \frac{1}{\sqrt{4\pi Et}} \exp\left(-\frac{(x-\bar{u}t)^2}{4Et}\right)$$

- where M is the mass of the pollutants and A is the cross-sectional area of the channel.
- The dispersion coefficient E can be evaluated from tracer experiments or derived from the theoretical equations, Fisher (1968).

Example 2.2

- As part of a renovation project, the reservoir is to be treated with CuSO₄ to remove the algae build-up. A fish nursery derives its water from the reservoir 700 m u/s of the Cu injection and has contracted you to determine, if the project will affect their operations. The fish nursery can accept a maximum Cu concentration of 0.0015 mg/l.
- After talking with the renovation contractor, you determine that: (i) The $CuSO_4$ is applied uniformly across the dam over a period of about one hour at spring season. (ii) 10 kg of Cu will be dissolved, (iii) the dam cross-sectional area A = 3000 m², (iv) E = 2 m²/s and (v) The average flow velocity past the fishery intake is 0.01 m/s.

- CuSO₄ is applied uniformly across the dam over a period of about one hour imply, we might model the copper contamination as an instantaneous source distributed evenly along the dam face.
- Because the project is scheduled for the spring turnover in the lake, the contaminant might be assumed to spread evenly in the vertical
- Advection or diffusion dominant: To evaluate the potential risks, the first step is to see how important diffusion is to the transport of Cu in the lake. This is done through the Peclet number, giving $Pe = uL/D = 0.01 \times 700 / 2 = 3.5$, which indicates diffusion is mildly important, and the potential for Cu to migrate upstream remains.

- Maximum concentration at intake: Because there is potential that copper will move upstream due mainly to diffusion, the concentration of Cu at the intake needs to be predicted.
- Taking the dam location at x = 0 and taking x positive downstream, the concentration at the intake (-700 m) is



- From the figure, the maximum allowable concentration is expected to be exceeded for about 1 day between the times t = 0.3 and t = 1.3 days.
- The maximum copper concentration at the intake will be about 0.0027 mg/l. Thus, the fish farm will have to take precautions to prevent contamination.
- What other factors do you think could increase or decrease the likelihood of Cu poisoning at the fish farm?

Transverse dispersion: depth-average mass-balance equation

- Since in most natural streams, width is considerably larger than the depth, the pollutants become uniformly spread over the depth much faster than they are spread uniformly across the width and hence it is customary to treat the motion of the pollutants in terms of the depth average version of the mass balance.
- E. R. Holley (1971) integrated **Eq. a** with negligible molecular diffusion over the depth and obtained the following equation:

$$h\left(\frac{\partial \bar{C}}{\partial t} + \bar{u}\frac{\partial \bar{C}}{\partial x} + \bar{v}\frac{\partial \bar{C}}{\partial y}\right) = \frac{\partial}{\partial x}\left(he_x\frac{\partial \bar{C}}{\partial x}\right) + \frac{\partial}{\partial y}\left(he_y\frac{\partial \bar{C}}{\partial y}\right)$$

• Where the over-bar now denotes the average over the depth and

The dispersion coefficients e_x and e_y are defined by the following expressions where in the effects of both the turbulent diffusion and those of the differential convection are taken care of.

$$\overline{u'C'} - \bar{\varepsilon}_x \frac{\partial \bar{C}}{\partial x} = e_x \frac{\partial \bar{C}}{\partial x} \text{ and } \overline{v'C'} - \bar{\varepsilon}_y \frac{\partial \bar{C}}{\partial z} = e_y \frac{\partial \bar{C}}{\partial y}$$

Depth-average mass-balance equation

 For a continuous injection of the pollutant when the concentration distribution becomes independent of time t, the longitudinal dispersion of pollutants is often neglected because of negligible concentration gradient in the longitudinal direction and hence the equation representing such a case becomes:

$$h\left(\bar{u}\frac{\partial\bar{c}}{\partial x} + \bar{v}\frac{\partial\bar{c}}{\partial y}\right) = \frac{\partial}{\partial y}\left(he_y\frac{\partial\bar{c}}{\partial y}\right)$$

• If the channel reach is straight, *v* becomes zero and if h is constant the above equation takes the form:

$$\bullet \bar{u} \frac{\partial \bar{C}}{\partial x} = \frac{\partial}{\partial y} \left(e_y \frac{\partial \bar{C}}{\partial y} \right)$$

1.4 Non-conservative pollutants

In the case of non-conservative pollutants, the mass-balance equation (Eq. a) has to be corrected for the production or the removal of the pollutants due to chemical reactions, change of state or transfer across the boundaries by adding an appropriate source or sink term S(x, y, z, t, C).

$$\begin{aligned} & \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} + w \frac{\partial c}{\partial z} = \\ & \frac{\partial}{\partial x} \left((D + \varepsilon_x) \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left((D + \varepsilon_y) \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left((D + \varepsilon_z) \frac{\partial C}{\partial z} \right) \\ & + S(x, y, z, t, C) \end{aligned}$$

 Some of the common examples of the non-conservative substances are dissolved oxygen and biochemical oxygen demand.

Longitudinal spreading of a non-conservative pollutant

- Consider the longitudinal spreading of a slug of a nonconservative pollutant injected instantaneously in a straight channel. The pollutant is assumed to undergo a first order reaction so that the rate of removal can be represented by kC where k is a reaction rate constant.
- In this case the transport of the pollutant can be represented by the one-dimensional dispersion equation with a sink term which is:

$$\frac{\partial \bar{C}}{\partial t} + \bar{u} \frac{\partial \bar{C}}{\partial x} = E \frac{\partial^2 \bar{C}}{\partial x^2} - k \bar{C}$$

• A solution of which is

$$\bar{C}(x,t) = \frac{M}{A} \frac{1}{\sqrt{4\pi Et}} \exp\left(-\frac{(x-\bar{u}t)^2 + 4Ekt^2}{4Et}\right)$$

Example 2.3

 A wastewater treatment plant (WWTP) discharges a constant flux of bacteria, m_b into a stream.

How does the concentration of bacteria change downstream of the WWTP due to the die-off of bacteria?

- The river is 20 cm deep and 20 m wide and has a flow rate of $Q = 1 \text{ m}^3/\text{s}$. The bacterial discharge is $m_b = 5 \times 10^{10}$ bacteria/s and the bacteria can be modeled with a first-order transformation equation with a rate constant of 0.8 day⁻¹.
- Assume that The bacteria are discharged well-mixed both vertically and horizontally at the discharge location.

- For first order reaction: $\frac{dC}{dt} = \pm kC \Rightarrow C(t) = C_0 e^{\pm kt}$
- For die-off bacteria the reaction constant is negative thus the solution is $C(t) = C_0 e^{-kt}$ where C_0 is the initial bacteria concentration and $k = 0.8/day = 9.25926 \times 10^{-6}/s$
- The initial concentration C₀ is the concentration at the discharge, which we can derive through the relationship

$$\mathbf{m}_{b0} = QC_0 \Rightarrow C_0 = \frac{m_{b0}}{Q} = \frac{5 \times 10^{10} bacteria/s}{1m^3/s} = 5 \times 10^{10} bacteria/m^3$$

• The next step is to covert the time t in our general solution to space x through the relationship x = ut, $u = 1/(0.2 \ge 20) = 0.25$ m/s

$$C(x) = C_0 e^{-k\frac{x}{u}} \Rightarrow C(x) = 5 \times 10^{10} \times e^{-9.25926 \times 10^{-6} \frac{x}{0.25}} = 5 \times 10^{10} \times e^{-3.7037 \times 10^{-5} x}$$

Example 2.4

- A 1000 gm of waste is accidentally released into a small stream. The stream channel has an average width of 40 m and an average depth of 2 m. The average water discharge (Q) in the stream is 40m³/sec, and the stream has a slope of 0.0001. Assuming that the waste is evenly distributed across the stream channel, estimate
 - The distribution of the waste as a function of distance downstream (using a maximum distance of 30 km) at 1, 3, 6, and 12 hours.
 - The waste activity (concentration) at a distance of 10km at 6 hours after the release.
- The waste has a half-life of 2.07 years. And $E = 50 \text{ m}^2/\text{s}$

- Cross-sectional area = Width x depth= $40m \ge 2m = 80 m^2$
- $Q = 40 \text{ m}^3/\text{s}$, v = Q/A = 40/80 = 0.5 m/s
- Calculate the rate constant, *k*, for the waste. For a first-order reaction, $\frac{dC}{dt} = -kt \Rightarrow C = C_0 e^{-kt}$
- where C is the concentration (or activity of waste) at time t, C₀ is the initial concentration (or activity), k is the decay rate constant, and t is time.
- At the half-life $(t_{1/2})$, one-half of the original concentration remains. Substitution of this into the equation above yields
- $C = C_0 e^{-kt} \Rightarrow 0.5C_0 = C_0 e^{-2.07k} \Rightarrow k = 0.338yr^{-1} = 1.07 \times 10^{-8} sec^{-1}$

• The plot showing the concentration profile at 12 hr is shown in Figure below. Using the velocity and time, we see the peak concentration should be at 21.5 km, which is observed in the Figure. The width of the Gaussian curve depends on the magnitude of E 0.003

magnitude of E. 0.0025 Calculate C(t) at 10 km onc g/m³ 0.002 downstream, after 6 hr 0.0015 0.001 (x = 10,000m and)0.0005 t = 6hr = 21,600 sec). 0 ANS. 0.00293 gm/m³ 0 20000 30000 10000 40000 **Distance d/s** $C(x,t) = \frac{M}{A} \frac{1}{\sqrt{4\pi Et}} \exp\left(-\frac{(x-\bar{u}t)^2 + 4Ekt^2}{4Et}\right)$

$$= \frac{1000}{80} \frac{1}{\sqrt{4\pi \times 50 \times 21600}} \exp\left(-\frac{(10000 - 0.5 \times 21600)^2 + 4 \times 50 \times 1.07 \times 10^{-8} \times 21600^2}{4 \times 50 \times 21600}\right)$$
$$= 0.00293$$

1.4.1 Self-purification and the oxygen balance

- Biological self-purification is the process in which organic wastes are broken down by the respiration of micro-organisms (aerobes) into stable end products.
- It is a biochemical oxidation process through which organic wastes are consumed leaving behind end products such as CO_2 , H_2O , PO_4 and NO_3 .
- Organic materials which can be broken down (i.e. are biodegradable) include natural materials such as simple sugars, starch, fats, proteins as well as more complex natural or synthetic compounds which are found in sewage or other wastes.
- This aerobic respiration, in which biochemical oxidation takes place uses the free dissolved oxygen (DO) in the water. Selfpurification of the river takes place by removing oxygen from the aquatic environment.
Dissolved oxygen, DO

- DO analysis measures the amount of gaseous oxygen (O₂) dissolved in an aqueous solution. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement), and as a product of photosynthesis.
- Degradable organic matter is broken down by microbes, usually with the help of oxygen, although in the absence of oxygen also anaerobic reactions are possible.
- Amount of organic waste load expressed as "Oxygen Demand":
- Theoretical oxygen demand, **ThOD**, from reaction with O_2 , *e.g.*: $C_2H_5OH + 3 O_2 \rightarrow 2 CO_2 + 3 H_2O$ (M.W.* of ethanol = 46)
- The OD of $C_2H_5OH = 3 \times \left(\frac{32}{46}\right) = \frac{2.08 \text{ mg O}_2/\text{mg ethanol}}{2}$
- (M.W. = molecular weight; M.W. of $C_2H_5OH = (2*12)+(5*1)+16+1=46$)

Exercise

• Calculate that the theoretical oxygen demand of:

•Glucose ($C_6H_{12}O_6$)

• ANS. = $1.07 \text{ g O}_2/\text{g glucose}$

Ethanal (C₂H₄O)
ANS. = 1.82 g O₂/g ethanal

Use the Periodic Table of Elements

Biochemical oxygen demand, BOD

- **BOD** is a procedure for determining the rate of uptake of DO by the micro-organisms in a body of water
- BOD measures the oxygen uptake by bacteria in a water sample at a temperature of 20°C over a period of five days in the dark. The sample is diluted with oxygen saturated de-ionized water, inoculating it with a fixed aliquot of microbial seed, measuring the DO and then sealing the sample to prevent further oxygen addition. The sample is kept at 20 °C for five days, in the dark to prevent addition of oxygen by photosynthesis, and the dissolved oxygen is measured again.
- The difference between the final DO and initial DO is the BOD or, BOD₅.
- BOD is a measure of organic content and gives an indication on how much oxygen would be required for microbial degradation.

Biochemical oxygen demand, BOD

- Except for pathogens, organic matter in water is generally not harmful in and of itself but may be considered as a pollutant because its bacterial decomposition generates a simultaneous oxygen depletion. Indeed, bacteria that feed on organic matter consume oxygen as part of their metabolism.
- The product of the decomposition is generally cellular material and CO₂. The more organic matter is present, the more bacteria feed on it, and the greater the O₂ depletion. For this reason, the amount of organic matter is directly related to O₂ depletion, and it is useful to measure the quantity of organic matter not in terms of its own mass but in terms of the mass of O₂ it will have removed by the time it is completely decomposed by bacteria. This quantity is called the BOD. Like DO, it is expressed in mg/L.
- BOD values can be extremely large in comparison to levels of DO. For example, BOD of untreated domestic sewage generally exceeds 200 mg/L and drops to 20–30 mg/L after a conventional wastewater treatment. Still, a value of 20 mg/L is high in comparison to the maximum, saturated value of DO (8 to 12 mg/L). This implies that even treated sewage must be diluted, lest it completely depletes the receiving stream from its oxygen.

Self purification

- When free oxygen is not available, anaerobes (sometimes known as 'facultative aerobes') can still break down simple sugars without the use of oxygen. Here, end products such as H_2S , NH_4 and CH_4 which may be toxic as well as foul smelling are often produced.
- If the supply of oxygen into the system is exceeded by the demand from respiration, an undesirable anaerobic state will occur.
- Thus, self-purification process is very closely tied with the DO content and with all the **sources and sinks** of oxygen in a river.
- Since DO is such a critical water quality parameter, the various processes affecting the DO shall be understood.
- NOTE: The water is 'purified' in the sense that the concentration of waste material has been reduced

Streeter and Phelps model



• Streeter and Phelps (1925), developed the classic oxygen balance equations by considering biochemical oxidation as the only sink and atmospheric re-aeration as the only source of oxygen.

- Mass Balance for the Model
 - •Rate O₂ accum. = rate O₂ in rate O₂ out + produced consumed

•Rate O_2 accum. = rate O_2 in $-0 + 0 - rate O_2$ consumed

- Kinetics: Both re-oxygenation and deoxygenation are 1st order
- **Deoxygenation**, L = BOD remaining at any time

•
$$\frac{dL}{dt} = -K_1 L$$
 for a first order reaction, $K_1 =$ deoxygenation constant, function of waste type and temperature

$$\frac{dL}{dt} = -K_1 t \Rightarrow L(t) = L_0 e^{-K_1 t}$$

•Where L_0 is the initial BOD

• Re-oxygenation:
$$\frac{dD}{dt} = K_2 D$$

Rate of re-oxygenation = K_2D , where D = (Cs - C)

 \bullet D = deficit in D.O. = saturation D.O. – D.O. in the water

• K_2 = re-oxygenation constant: There are many correlations for this. The simplest one, used here, is from O'Connor and Dobbins, 1958 Where

•
$$K_2 = \frac{3.9v^{1/2} ([1.025]^{(T-20)})^{1/2}}{H^{3/2}}$$

- Typical values for K₂ at 20 °C, in d⁻¹ unit are as follows:
 - •Small ponds and back water 0.10 0.23
 - •Sluggish streams and large lakes 0.23 0.35
 - •Large streams with low velocity 0.35 0.46

- -T = temperature of water, °C
- -H = average depth of flow, m
- -v = mean stream velocity, m/s
 - Large streams at normal velocity 0.46 0.69
 - Swift streams 0.69 1.15
 - Rapids and waterfalls > 1.15

- Combining the kinetics (re-oxygenation and deoxygenation)
- Net rate of change of oxygen deficiency, dD/dt

$$\frac{dD}{dt} = K_1 L - K_2 D, where \Rightarrow L = L_0 e^{-K_1 t}$$

$$\Rightarrow D = \frac{K_1 L_0}{K_2 - K_1} (e^{-K_1 t} - e^{-K_2 t}) + D_0 e^{-K_2 t}$$
Mothod of variation of parameters: $\frac{dD}{dt} + K_2 D = K_1 L$

- Method of variation of parameters: $\overline{dt} + K_2 D = K$
- Set $K_1 L = 0$, the differential equation reduces to

$$\frac{dD}{dt} + K_2 D = 0 \Rightarrow D = c e^{-K_2 t}$$

• Replace the parameter *c* by a function of *t*, say u(t). Therefore we suppose that a solution of the equation is given by: $D = u(t)e^{-K_2t}$

• It can be observed that the minimum value, D_c is achieved when $\frac{dD}{dt} = 0$

$$\frac{dD}{dt} = 0 \Rightarrow K_1 L_0 e^{-K_1 t} - K_2 D = 0 \Rightarrow D_c = \frac{K_1}{K_2} L_0 e^{-K_1 t}$$

• Substituting this last equation in the first, when $D = D_c$ and solving for $t = t_c$: $t_c = \frac{1}{K_2 - K_1} \ln \left\{ \frac{K_2}{K_1} \left[1 - \frac{D_o(K_2 - K_1)}{K_1 L_o} \right] \right\}$



Example 2.5

- Wastewater mixes with a river resulting in a
 - **BOD** = 10.9 mg/L,
 - •DO = 7.6 mg/L
 - The mixture has a temperature = $20 \degree C$
 - Deoxygenation const.= 0.2 day⁻¹
 - •Average flow = 0.3 m/s,
 - •Average depth = 3.0 m
 - •DO saturated = 9.1 mg/L
- Find the time and distance downstream at which the oxygen deficit is a maximum
- Find the minimum value of DO

Solution

- Initial Deficit: $D_0 = 9.1 7.6 = 1.5 \text{ mg/L}$
- (Now given, but could be calculated from proportional mix of river DO, presumably saturated, and DO of wastewater, presumably zero)
- Estimate the reaeration constant:

$$K_{2} = \frac{3.9v^{1/2} ([1.025]^{(T-20)})^{1/2}}{H^{3/2}} = \frac{3.9 \times 0.3^{1/2} ([1.025]^{(20-20)})^{1/2}}{3^{3/2}} = 0.41d^{-1}$$

$$t_{c} = \frac{1}{K_{2}-K_{1}} \ln \left\{ \frac{K_{2}}{K_{1}} \left[1 - \frac{D_{o}(K_{2}-K_{1})}{K_{1}L_{o}} \right] \right\} = \frac{1}{(0.41-0.2)} \ln \left\{ \frac{0.41}{0.2} \left[1 - \frac{1.5(0.41-0.2)}{0.2 \times 10.9} \right] \right\} = 2.67day$$

$$x_{c} = vt_{c} = 0.3m/s \times 86,400s/day \times 2.67days = 69,300m$$

$$D_{c} = \frac{K_{1}}{K_{2}}L_{o}e^{-k_{1}t} = \frac{0.2}{0.41} (10.9 \text{ mg/L}) e^{-(0.2\text{day}^{-1})(2.67\text{days})} = 3.1 \text{ mg/L}$$

• The minimum DO value is 9.1-3.1 = 6 mg/L

Sources and sinks of oxygen

- Addition of BOD by local runoff
- Removal of BOD by sedimentation or adsorption;
- Addition of BOD by the scour of bottom deposits or by the diffusion of partly decomposed organic products from the benthal layer into the water above;
- Removal of oxygen from the water by diffusion into the benthal layer to satisfy the oxygen demand in the aerobic zone of this layer (important in shallow stream with depth < 2m)
- Removal of oxygen from the water by- the purging action of gases rising from the benthal layer
- Addition and removal of oxygen by the photosynthetic action and respiration of plankton and fixed plants

Evaluation of the source-sink terms

- In general, the dominant processes which ought to be considered in the oxygen balance of a river are the following:
 - Immediate chemical oxygen demand
 - The BOD of the wastes disposed in the water (S&P)
 - Oxygen demand of the bottom deposits
 - Oxygen required for plant respiration
 - •Oxygen produced by plant photosynthesis
 - •Oxygen gained from atmospheric re-aeration (S&P)

Evaluation of the source-sink terms

- Referring to equation for the mass-balance of a nonconservative substance, the equation for the DO distribution for the case of a straight uniform reach and negligible molecular diffusion is: $\frac{\partial \bar{c}}{\partial t} + u \frac{\partial \bar{c}}{\partial x} = \frac{\partial}{\partial x} \left(\varepsilon_x \frac{\partial \bar{c}}{\partial x} \right) + \sum_i S_i$
- where C bar is the depth average DO concentration and S_i represents the individual source and sink DO terms.
- Immediate chemical oxygen demand

Many types of effluents contain substances which are fairly quickly oxidized by molecular oxygen. These substances exert a load on the DO content and the amount of oxygen required for the oxidation is called the immediate chemical oxygen demand.

Biochemical oxygen demand (BOD)

- It is usually assumed that the rate of biochemical oxidation is a first order process, i.e. the oxidation rate is proportional to the amount of waste remaining in the water.
- The net rate of sedimentation and scour is also generally assumed to be proportional to the amount of BOD present.
- Therefore, the equation for the distribution of BOD can be written as: $\frac{\partial \bar{L}}{\partial t} + u \frac{\partial \bar{L}}{\partial x} = \frac{\partial}{\partial x} \left(\varepsilon_x \frac{\partial \bar{L}}{\partial x} \right) - K_1 \bar{L} - K_3 \bar{L}$
- where L $_{bar}$ = average BOD concentration in the water; K₁ = rate constant for the biochemical oxidation; K₃ = rate constant for the net rate of settling and re-suspension of BOD.
- Values for K₁ can vary from 0.01/day to 0.3/day depending on the type of waste and the degree of stabilization (Camp, 1963).

BOD

- The coefficient K₃ for the settling and re-suspension of BOD has to be determined from BOD profile measurements.
- K₃ is usually difficult to predict because

•Settling and re-suspension are governed by the flow conditions and particle size, however effluent might flocculates into different sizes.

- •Under steady state conditions, with no sediment build-up, the amount of settling and scour should be equal. However, the material settling and that being scoured may not have the same BOD concentration.
- The coefficient K_3 is usually just an average for the river reach.
- Dobbins (1964) has indicated how K₃ can be calculated from the measured BOD profile, provided that K₁ has been determined from laboratory measurements.

Plant respiration and photosynthesis

- Aquatic plants, benthic algae and phytoplankton all consume oxygen for their respiration (24hr/day). Photosynthesis release free molecular oxygen (daylight hours),
- Therefore, DO levels tend to be highest in mid-afternoon and lowest during the early hours of the morning.
- The photosynthesis production of oxygen depends on the light intensity, the optical density of water and the quantity of plants.
- Even though environmental conditions were suitable for algal growth and a high level of photosynthesis, turbidity may reduce light transmission so that the oxygen production will be low.
- Nevertheless, the processes of photosynthesis and respiration can be very important factors and should be included in the DO balance.

Atmospheric re-aeration

- Re-aeration is the process of absorption of atmospheric oxygen into the water.
- It is one of the most important factors controlling the waste assimilative capacity of a river 'because photosynthesis and reaeration are the only two sources of oxygen replenishment, and photosynthesis can take place only when there is sunlight.
- The water surface which is in contact with the atmosphere becomes saturated with oxygen in a very short time.
- Once the surface is saturated, the DO has to find its way into the body of the fluid before more oxygen can be absorbed.
- In the region very close to the surface, viscosity dominates and oxygen is transferred into the liquid below it by molecular diffusion which is a very slow process.

Atmospheric re-aeration

- It is generally agreed that the rate of oxygen absorption is proportional to the oxygen deficit, i.e. the difference between the saturation concentration and the actual DO concentration.
- The proportionality constant is called the re-aeration coefficient K_2 . The source term, S_i , representing re-aeration is: $K_2(C_s C)$ where C_s is the saturation DO concentration.
- C_s is a function of temperature and may be calculated approximately from the following empirical equation:

 $C_s = 14.541233 - 0.3928026T + 0.00732326T^2 - 0.00006629T^3$

■Where T is stream temperature (°C).

• K₂ is not a constant for all flows. It depends on channel slope, bottom roughness, flow velocity and wind. All these factors affect the turbulence near the water surface which controls the rate of oxygen absorption.

Oxygen balance

- The solution of the DO concentration is a little more complicated because of the BOD term
- Analytical solutions are obtained only for one-dimensional case, considering the whole cross-section of the river to be well mixed.
- Dobbins (1964) considered removal of BOD by sedimentation or absorption, the addition of BOD along the reach as well as the BOD reaction rate. The BOD profile equation is:

$$u \frac{dL}{dx} = E \frac{d^2L}{dx^2} - (K_1 + K_3)L + L_a$$

• where L_a is the rate of addition of BOD along the reach. The solution is given by:

•
$$L = L_o e^{(mx)} + \frac{L_a}{K_1 + K_3} (1 - e^{(mx)}); m = \frac{u - \sqrt{(u^2 + 4(K_1 + K_3)E)}}{2E}$$

•
$$L = L_o$$
 at $x = 0$. and $L = 0$ a $x = \infty$

Oxygen Balance

• This value for L is then used in the DO balance equation :

•
$$u\frac{dC}{dx} = E\frac{d^2C}{dx^2} + K_2(C_s - C) - K_1L - D_B$$

- where D_B stands for the net effect of plant photosynthesis and respiration and benthal demand.
- The solution, subject to the boundary conditions that $C = C_0$ at x = 0 and equilibrium between atmospheric re-aeration and photosynthesis and benthal demand at $x = \infty$, is given by:

•
$$C_s - C = \frac{K_1 \left(L_o - \frac{L_a}{K_1 + K_3} \right) \left(e^{(mx)} - e^{(rx)} \right)}{K_2 - (K_1 + K_3)} + (C_s - C_o) e^{(rx)} + K_1 \left(\frac{D_B}{K_2} + \frac{K_1 L_a}{K_2 (K_1 + K_3)} \right) \left(1 - e^{(rx)} \right)$$

• Where $r = \frac{u - \sqrt{(u^2 + 4K_2 E)}}{2E}$

Oxygen Balance

- The above Equation is valid when the BOD is reasonably well mixed throughout.
- However, outfall discharges are generally located at one bank or at some location in the stream and are not initially well mixed across the section. In this case the two-dimensional equations have to be solved.
- Holley (1973) compared the one-dimensional and twodimensional distributions and found that, except in cases of relatively fast transverse mixing, the two-dimensional solution gave smaller DO concentrations as low as onefourth of those calculated by the one-dimensional solution.
- Thus ecologically sensitive stretch of river such as spawning grounds, a two-dimensional DO balance should be used.

Example 2.6

- Redo example 2.5 take $K_3 = 0$ and $E = 2 \text{ m}^2/\text{s}$
- For the example since there is no is the rate of addition of BOD along the reach, thus $L_a = 0$.
- The net effect of plant photosynthesis and respiration and benthal demand balances each other.
- The solution is given by:

•
$$L = L_0 e^{(mx)} + \frac{L_a}{K_1 + K_3} (1 - e^{(mx)}); m = \frac{u - \sqrt{(u^2 + 4(K_1 + K_3)E)}}{2E}$$

• Where $K_1 = 0.2/day = 2.013 \times 10^{-6} \text{ s}^{-1}$ and $L = L_o at x = 0$.

•
$$L = L_0 e^{(mx)}$$
;
• $m = \frac{u - \sqrt{(u^2 + 4(K_1)E)}}{2E} = \frac{0.3 - \sqrt{(0.3^2 + 4 \times 2.013 \times 10^{-6} \times 2)}}{2 \times 2} = -6.7093 \times 10^{-6}$
• $L = L_0 e^{(mx)} = 10.9 \times e^{(-6.7093 \times 10^{-6}x)}$

Solution

•
$$C_s - C = \frac{K_1(L_0)(e^{(mx)} - e^{(rx)})}{K_2 - (K_1)} + (C_s - C_0)e^{(rx)} + K_1\left(\frac{D_B}{K_2}\right)\left(1 - e^{(rx)}\right)$$

• $K_2 = 0.41 day^1 = 4.13 \times 10^{-6} \text{ s}^1$

• Where
$$r = \frac{u - \sqrt{(u^2 + 4K_2E)}}{\frac{2E}{2}} = \frac{0.3 - \sqrt{(0.3^2 + 4 \times 4.13 \times 10^{-6} \times 2)}}{2 \times 2} = -1.3753 \times 10^{-5}$$

• 9.1-
$$C = \frac{2.013 \times 10^{-6} \times 10.9 \times \left(e^{(-6.7093 \times 10^{-6}x)} - e^{(-1.3753 \times 10^{-5}x)}\right)}{4.13 \times 10^{-6} - 2.013 \times 10^{-6}} + (9.1 - 7.6)e^{(-1.3753 \times 10^{-5}x)}$$

• 9.1 –
$$C = 10.381e^{(-6.7093 \times 10^{-6}x)} - 8.881e^{(-1.3753 \times 10^{-5}x)}$$

Solution



• The maximum deficit (3.1 mg/lit) occur at a distance of 79750 m, which is larger than the S&P model (69300m). WHY?

2. Transport in lake and reservoirs

- Lakes and reservoirs are typically standing waters. They exhibit a range of surface areas, volumes, depths and water retention times.
- Many lakes have enormously long retention times, often measured in hundreds of years while most reservoirs have retention times considerably less.
- Many reservoirs with very short retention times possess some of the characteristics of rivers, e.g. horizontal gradients in chemical parameters and water currents. Orlob (1969) devised an index to describe how close a body of water is to the riverine or lacustrine situation. The higher the value of the index the closer the body of water is to behaving like a river and not exhibiting thermal stratification.

$$Fr = 320 \frac{LQ}{DV}$$

where Fr = Stratification index (0.318)

L = Length of water body (m)

D = Average depth (m)

Q = Average discharge from water body (m/s)

$$V = Volume (m^3)$$

Transport in Lakes and Reservoirs

- There are two main types of reservoirs:
- ¹ Those created by damming a river and flooding its valley.
- ^{2.} Those created by constructing an artificial basin and filled by pumping or gravitation.
- Both types of reservoir can be used for several purposes, e.g.
- Reservoirs primarily intended to store water in times of plenty
 for use for drinking or irrigation during times of shortage. Filled
 during the wet season and drawn down during the dry season.
- 2. Flood control reservoirs: it may be filled in a few days.
- ^{3.} Pumped storage reservoirs: may be filled and emptied on a 24hr.
- 4. Hydropower reservoirs are usually kept at top water level so as to ensure constant power generation.
- 5. Reservoirs for recreation usually require a constant water level.

Thermal stratification

- Hutchinson and Loeffler (1956) have classified lakes according to their thermal behavior and recognized six main categories:
- *Cold Monomictic* usually polar, sub-polar or high mountain lakes with full circulation only in summer usually being free from ice for only a short period.
- 2. *Dimictic* temperate lakes with full circulation in spring and autumn, stratified in summer and winter.
- *Warm Monomictic* sub-tropical lakes, stratified for most of the year, full circulation in early winter.
- Oligomictic small or very deep lakes where a very small temperature difference between top and bottom surfaces maintains stable stratification. The lake circulates only at rare, irregular intervals when abnormal cold spells occur.
- *Cold Polymictic* lakes at great altitudes, no permanent stratification develops, mixing at night.
- *Warm Polymictic* tropical lakes receiving solar radiation during the day but back-radiating at night allowing nocturnal mixing.



FIGURE 6-7 Schematic arrangement of thermal lake types with latitude and altitude. Black dots: cold monomictic; black-and-white horizontal bars: transitional regions; horizontal lines: dimictic; crossed lines: transitional regions; vertical lines: warm monomictic. The two equatorial types occupy the unshaded areas labeled oligomictic and polymictic, separated by a region of mixed types, mainly variants of the warm monomictic type (broken vertical lines). (Modified from Hutchinson and Löffler, 1956.)

Water movement

- In general, current systems in lakes are of two kinds.
- The first is periodic and generally due to the disturbance of the lake by wind forces or atmospheric pressure causing an oscillation of the lake or part of it.
 - •If a wind that has piled up water at one end of the lake suddenly dies down, a current will flow momentarily restoring the lake to its former level. The current will not have lost its energy and will continue, piling up water at the opposite end of the lake. This current is called *seiche*
 - •*Seiche* constitutes an oscillation about a nodal line. As with other oscillating systems there is a tendency for harmonics to form and *seiches* may be multi-nodal.

Water movement

- The second kind of current is non-periodic, generated by external forces namely: *the influent-effluent system of the lake, unequal heating, the entry of dissolved material from the sediments and variations in atmospheric pressure and winds.*
- Special problems arise in very large lakes where the Coriolis force (an inertial current imposed by the earth's rotation) is of significant influence.
- Special problems with the behavior of incoming water may also arise in reservoirs especially in the narrow, elongated river impoundment. If there is a pronounced temperature (and density) difference between the influent and the reservoir, the incoming water may plume across the surface or flow along the bottom.

Water movement

- Further problems due to temperature may arise depending on the position of the reservoir outlet. If the reservoir outlet is close to the surface, the river downstream will receive warm water in summer (Epilimnetic) and cold in winter. From deep stratified reservoirs with outlets at the bottom, cold hypolimnetic water may be released continuously thus providing a habitat downstream for cold water adapted fish.
- In pumped storage reservoirs, temperature regime and stratification depend to a considerable degree on the mode of operation. Conditions in shallow reservoirs for drinking water supply correspond to those in natural lakes. In deep pumped storage reservoirs used for power generation, there may be no stratification because of the rapid flow through of water.

Dispersion of pollutants

- When a 'batch' of pollutant is released into a turbulent lakecurrent, it is subject to two important physical effects of water movement: transport and diffusion. The former is bulk bodily movement of a parcel of pollutant due to lake mean currents, whereas-the latter is the spreading of the pollutant parcel as a consequence of turbulence and current shear naturally associated with the lake currents.
- The concentration field C(x, t) within a diffusing pollutant 'cloud' or a plume in the lake environment is a random variable: it varies irregularly in both space and time.
- Iso-concentration contours mapped from an individual diffusing fluorescent dye patch usually have irregular shapes and the diffusing dye patch grows in a highly complex manner.

Dispersion of pollutant

- Many pollutants retain their chemical composition in the lake environment for long periods of time and are called 'conservative'.
- Because the 'total mass' is conserved, the pollutant concentration at the center of the patch must decrease in time
- The *two* important characteristics of diffusing plume or patch are the spread defined in terms of the standard deviations in the three dimensions and the maximum concentration.
- These two dispersion characteristics are related through the conservation of mass. Therefore, in predicting the dispersion of a pollutant patch or plume, we need only to focus on the rate of growth of the diffusing plume or patch under lake environmental conditions. Empirical diffusion characteristics are indeed related to this important parameter.

Diffusion processes

- Several conceptual models of turbulent diffusion exist which are directly applicable to describe the transport and dispersion of pollutants discharged into a lake, and, in general form, these are similar to the differential equation models described for dispersion, in river systems but extended to the 3D case.
- Turbulent fluctuations of current velocity may be visualized as comprising many eddies of different sizes. These eddies are radically different in horizontal as compared to vertical direction.
- When a diffusing patch or plume of pollutant comes under the influence of an eddy, it simply advects with the eddy and does disperse appreciably. However, eddies which are comparable in size to that of the patch lead to effective dispersion.
- This process, referred to as 'eddy diffusion', goes on as long as there are eddies of the required size present in the lake currents.

Diffusion processes

- Dispersion of a pollutant cloud in the lake environment is caused by yet another process known as 'shear diffusion' due to the vertical and horizontal shears associated with the lake currents.
- An interaction of current shear and eddy diffusion results in an apparent dispersion of pollutant clouds. The effect of current shear is particularly important in large lakes where diffusing clouds of pollutant often become large enough for their *mean* velocities to be significantly different from the leading edge to the trailing edge.
- Clearly, such velocity differences distort the shape of the cloud. The immediate effect of such distortion is a sharpening of the concentration differences existing in the cloud.

Example 2.7

- A lake of 1000 m³ can be broken into a surface layer of 500 m³ and two deeper layers of equal size. The top layer is fed by a contaminated stream with concentration 5g/liter, which flows in at a rate of 20 m³/hr. It is drained by a similar stream. The surface and middle layer have a turbulent exchange rate of 5 m³/hr, while the middle and lower layer have an exchange rate of 1 m³/hr. Given enough time, what will the concentration profile in the lake look like?
- Solution:



Example: Mass balance equations

• For the first Layer (Layer 1)

$$\begin{aligned} & \frac{d}{dt}(C_1V_1) = Q_{in}C_{in} - Q_{out}C_{out} - Q_{evap}C_{evap} + \\ & Q_{rain}C_{rain} - Q_{1\to 2}C_1 + Q_{2\to 1}C_2 \\ & \bullet V_1 \frac{dC_1}{dt} = Q_{in}(C_{in} - C_{out}) - Q_{evap} \times 0 + Q_{Rain} \times 0 - \\ & Q_{1\to 2}(C_1 - C_2) \\ & \bullet 500 \frac{dC_1}{dt} = 20 \times (5 - C_1) - 5 \times (C_1 - C_2) \\ & \bullet \frac{dC_1}{dt} = \frac{100 - 25C_1 + 5C_2}{500} \end{aligned}$$

Example: Mass balance equations

• For the second Layer (Layer 2)

$$\begin{aligned} & \frac{d}{dt}(C_2V_2) = Q_{in}C_{in} - Q_{out}C_{out} + Q_{1\to 2}C_1 - Q_{2\to 1}C_2 \\ & + Q_{3\to 2}C_3 - Q_{2\to 3}C_2 \end{aligned}$$
$$\begin{aligned} & V_2\frac{dC_2}{dt} = 0 \times 0 - 0 \times 0 + Q_{1\to 2}(C_1 - C_2) + Q_{3\to 2}(C_3 - C_2) \end{aligned}$$

$$-250 \frac{dC_2}{dt} = 5 \times (C_1 - C_2) + 1 \times (C_3 - C_2)$$
$$-\frac{dC_2}{dt} = \frac{5C_1 - 6C_2 + C_3}{250}$$

Example: Mass balance equations

• For the third Layer (Layer 3)

$$\begin{aligned} & -\frac{d}{dt}(C_3V_3) = Q_{in}C_{in} - Q_{out}C_{out} - Q_{3\to 2}C_3 + Q_{2\to 3}C_2 \\ & -V_2\frac{dC_3}{dt} = 0 \times 0 - 0 \times 0 - Q_{3\to 2}(C_3 - C_2) \\ & -250\frac{dC_3}{dt} = -1 \times (C_3 - C_2) \\ & -\frac{dC_3}{dt} = \frac{C_2 - C_3}{250} \end{aligned}$$

• For steady state

$$100 - 25C_1 + 5C_2 = 0 C_1 = 5g/lit C_2 = 5g/lit C_2 = 5g/lit C_3 = 5g/lit C_3$$