

Chapter 6 Mixing of Decaying Substances

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6.6 Modeling Toxic Substances

Objectives

6.1 Non-Conservative Pollutants

6.1.1 Category of Non-Conservative Pollutants

1) Toxic Substance

- Metals: mercury, cadmium, lead
- Industrial chemicals: toluene, benzenes, phenols, PCB
- Hydrocarbons: PAH (polycyclic aromatic hydrocarbons)
- Agricultural chemicals: pesticides, herbicides, DDT
- Radioactive substances

2) BOD-DO coupled system

3) Temperature

4) Suspended Solids

5) Bacteria and pathogens

6) Nutrients

7) Oil

[Cf] Conservative pollutants

- one which does not undergo any chemical or biochemical changes in transport
- no loss due to chemical reactions or biochemical degradation
- salt, chloride, total dissolved solids, some metals

6.1.2 Transport of Non-Conservative Pollutants

(1) Toxic Substance

Physio-chemical phases of the transport of toxic substances:

- loss of the chemical due to biodegradation, volatilization, photolysis, and other chemical and bio-chemical reactions
- sorption and desorption between dissolved and particulate forms in the water column and bed sediment
- settling and resuspension mechanisms of particulates between water column and bed sediment

Assume only loss of the chemical

$$\frac{\partial(hC)}{\partial t} + \frac{\partial}{\partial x}(uCh) + \frac{\partial}{\partial y}(vCh) = \nabla \cdot (hD\nabla C) + hS$$

where S = sink/source term

Assume first-order decay

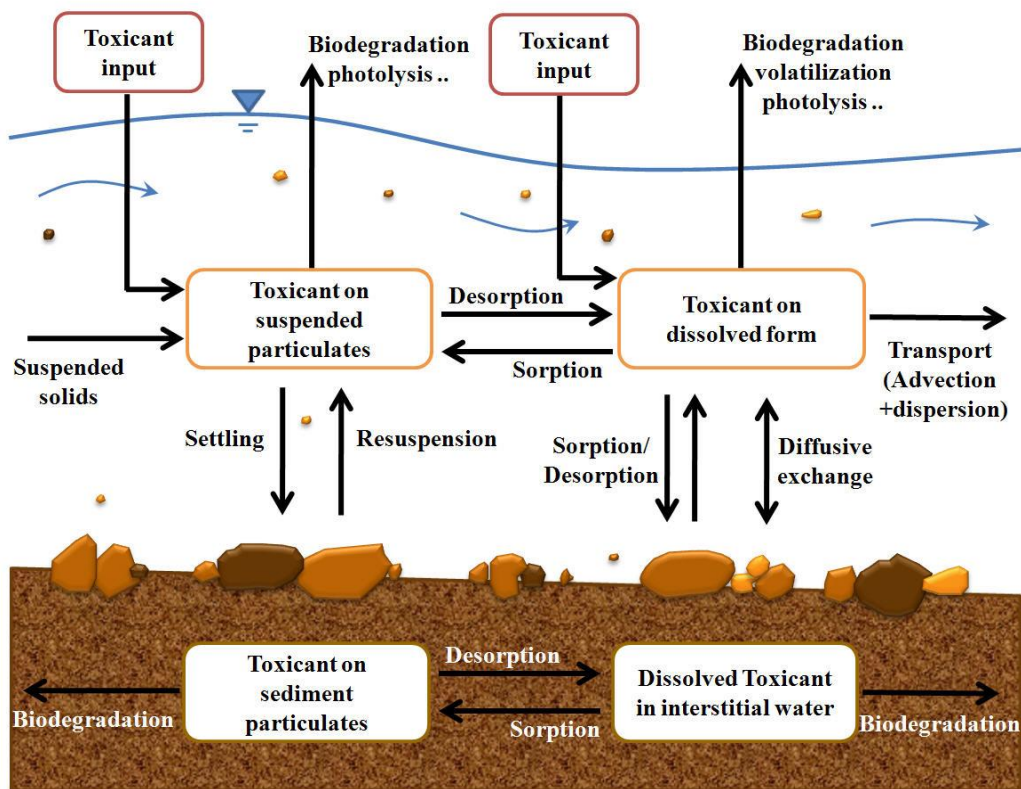
- decay rate is proportional to the amount of material present

$$\frac{dC}{dt} = -kC = S$$

where C = mass/volume; S = mass/(volume · time); k = 1/time = decay rate

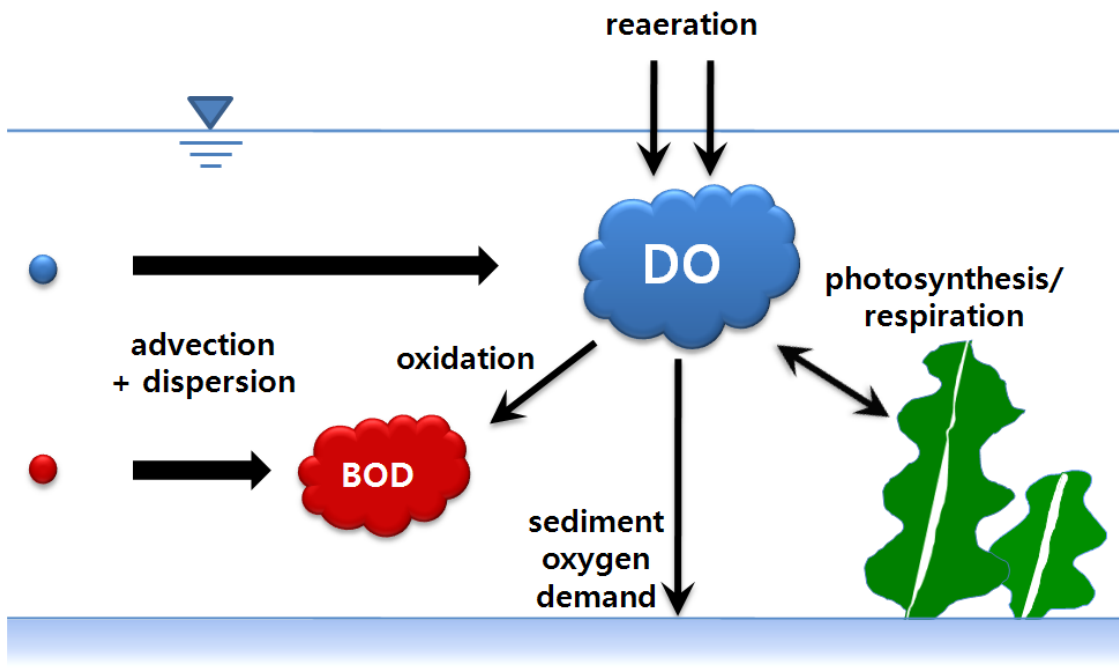
- Rate of disappearance of BOD due to biodegradation
- Radioactive substance also decay in strength in this way
- Coliform bacteria and pathogens die away with a rate of first-order decay

$$\frac{\partial(hC)}{\partial t} + \frac{\partial}{\partial x}(uCh) + \frac{\partial}{\partial y}(vCh) = \nabla \cdot (hD\nabla C) - khC$$



(2) BOD-DO

- Linked materials
- Behavior of one material depends upon the amount of another- Conc. of dissolved oxygen depends not only on transport of DO but also on the amount of BOD present
- Biodegradable substances undergo biochemical reactions
- Oxygen is used up in aerobic decomposition



(3) Heat transport

$$\frac{\partial hT}{\partial t} + \frac{\partial}{\partial x}(uTh) + \frac{\partial}{\partial y}(vTh) = \nabla \cdot (hD\nabla T) + hS$$

$$S = \frac{dT}{dt} = \frac{q_{net}}{\rho c_p h} = \frac{K(T - T_e)}{\rho c_p h}$$

K = atmospheric heat exchange coefficient ($W / m^2 \text{ } ^\circ C$)

c_p = specific heat of water

T_e = equilibrium temperature

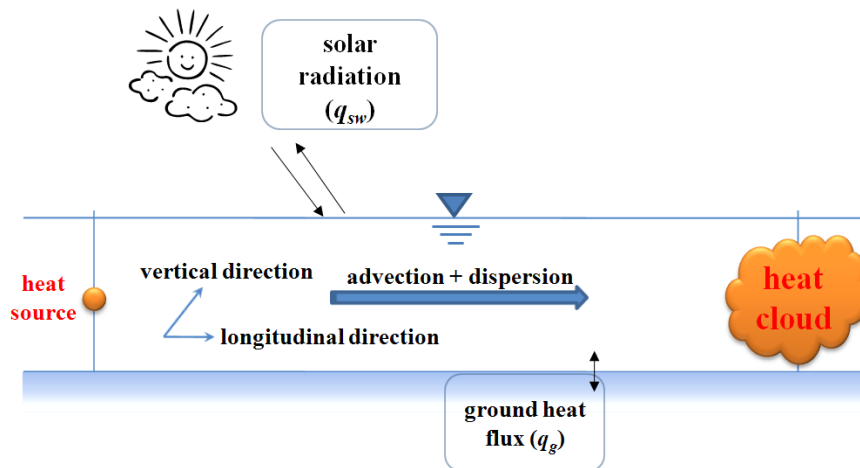
= temperature that a body of water would reach if all meteorological conditions were constant in time

Assume that u, v, h satisfy the continuity eq.

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{1}{h} \nabla \cdot (hD\nabla T) + \frac{A}{\rho c_p} (T - T_e)$$

$$T_e = T_d + \frac{q_{sw}}{K}$$

T_e = dew point temperature



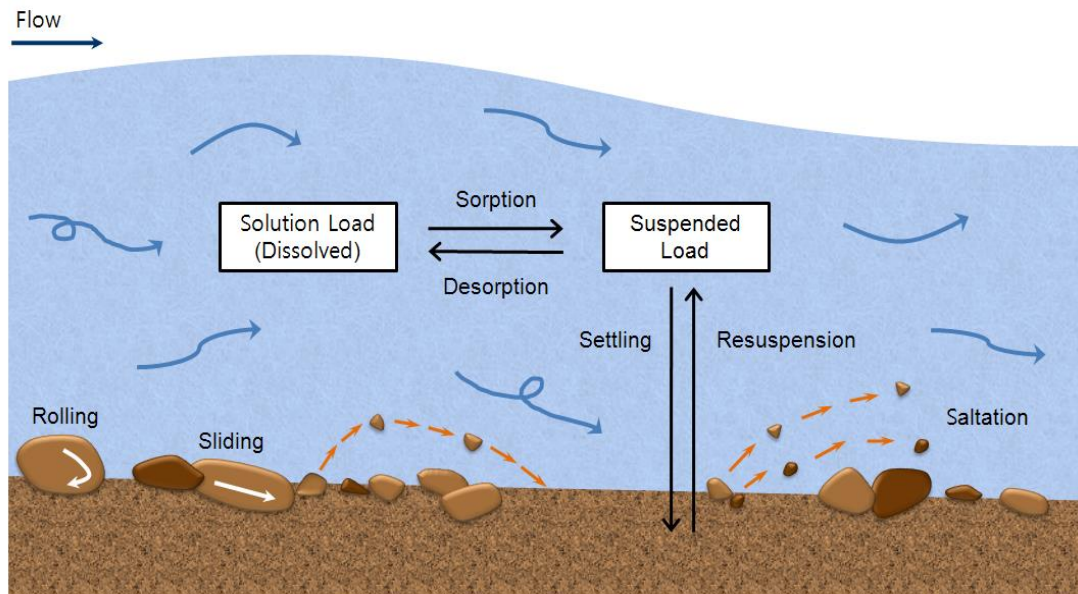
(4) Suspended Solids

Suspended solids= suspended sediments + particulate forms in the water column

$$\frac{\partial(hC)}{\partial t} + \frac{\partial}{\partial x}(uCh) + \frac{\partial}{\partial y}(vCh) = \nabla \cdot (hD\nabla C) + hS$$

$$S = \frac{W_s(C_{eq} - C)}{h}$$

$$C_{eq} = \frac{G_{gr} D \rho_s}{\rho h}$$



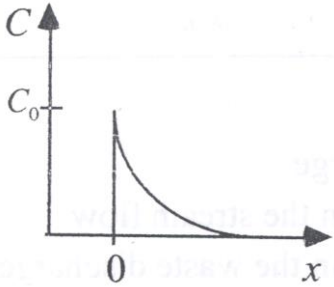
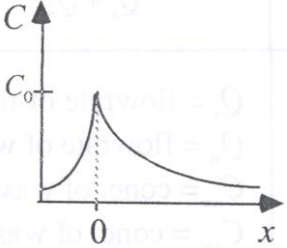
6.2 Analytical Solutions for Non-Conservative Pollutants

6.2.1 Steady state equations and solutions

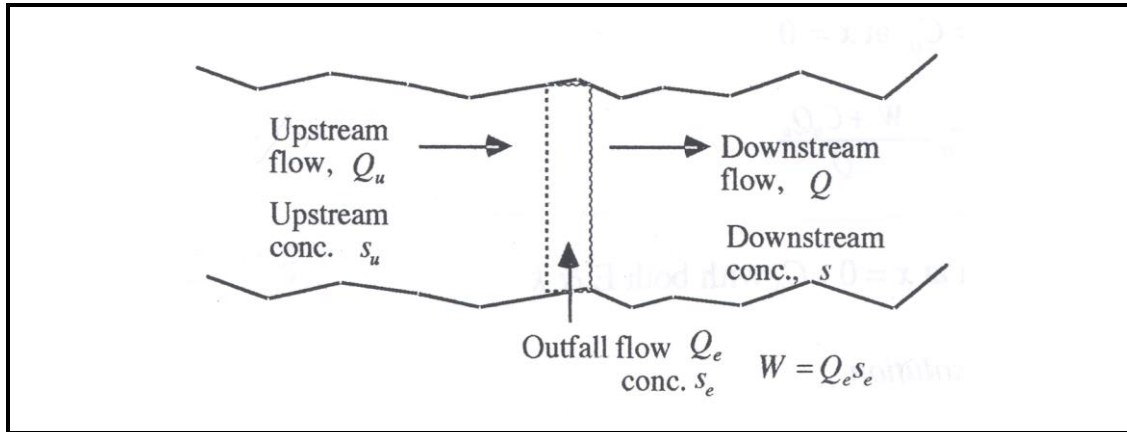
- Pollutant discharges are nearly constant over time (continuous discharge)
- Concentration in the stream will reach a steady state condition soon after the discharge starts.

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

I. Conservative Pollutant		
Item	W/O Dispersion (Case 1)	W/ Dispersion (Case 2)
G.E.	$0 = u \frac{\partial C}{\partial x}$	$0 = -u \frac{\partial C}{\partial x} + E \frac{\partial^2 C}{\partial x^2}$
B.C.'s	$C(0) = C_0$ - continuous discharge	$C(0) = C_0$ - continuous discharge
Solutions	$C(x) = C_0, x \geq 0$ $C_0 = \frac{Q_s C_{ws} + Q_w C_{ww}}{Q_s + Q_w}$	$C = C_0 \exp\left(\frac{u}{E} x\right), x < 0$ $C = C_0, (x \geq 0)$
	Q_s = flowrate of the stream; Q_w = flowrate of waste discharge C_{ws} = conc. of waste material in the stream flow C_{ww} = conc. of waste material in the waste discharge	
Graphics		

II. Non-conservative Pollutant		
Item	W/O Dispersion (Case 3)	W/ Dispersion (Case 4)
G.E.	$0 = -u \frac{\partial C}{\partial x} - kC$	$0 = -u \frac{\partial C}{\partial x} + E \frac{\partial^2 C}{\partial x^2} - kC$
B.C.'s	$C(0) = C_0$ $C_0 = \frac{W}{Q} = \frac{Q_s C_{ws} + Q_w C_{ww}}{Q_s + Q_w}$	$C(-\infty) = 0$ $C(\infty) = 0$ $C(0) = C_0$ $C_0 = \frac{W}{Q} \frac{1}{\alpha}$
Solutions	$C(x) = C_0 \exp(-\frac{k}{u} x), x \geq 0$	$C(x) = C_0 \exp\left[\frac{u}{2E}(1+\alpha)x\right], x \leq 0$ $C(x) = C_0 \exp\left[\frac{u}{2E}(1-\alpha)x\right], x \geq 0$ $\alpha = \sqrt{1 + \frac{4kE}{u^2}}$
Graphics		

- Boundary condition at the outfall



1) Conservative substance

Consider mass balance at discharge point (outfall)

Mass rate of substance upstream + mass rate added by outfall

= mass rate of substance immediately downstream from outfall assuming complete mixing

(using midstream discharge of diffuser)

$$Q_u s_u + Q_e s_e = Qs \quad (a)$$

$$W = Q_e s_e = \text{input waste load [M/T]} \quad (b)$$

[Re] mass rate = flow rate \times concentration

Flow continuity

$$Q_u + Q_e = Q \quad (c)$$

Combine (a) ~ (c)

$$s = \frac{Q_u s_u + Q_e s_e}{Q} = \frac{Q_u s_u + W}{Q}$$

If $s_u = 0$

Then $s = \frac{W}{Q}$

Thus, boundary condition at the outfall is give as

$$C = C_0 = \frac{W + C_u Q_u}{Q} \text{ at } x = 0$$

2) Non-conservative substance

Derive general solution to the governing equation below

$$0 = -u \frac{\partial C}{\partial x} + E \frac{\partial^2 C}{\partial x^2} - kC \tag{6.32}$$

This G.E. can be regarded as second order ordinary differential equation since C is a function of x .

It is a kind of characteristic equation.

Thus, we try a solution of the form $C = e^{mx}$, then $\frac{\partial C}{\partial x} = me^{mx}$ and $\frac{\partial^2 C}{\partial x^2} = m^2 e^{mx}$.

Applying these equations into G.E. gives characteristic equation as follow.

$$0 = -u(me^{mx}) + E(m^2e^{mx}) - k(e^{mx}) = e^{mx}(Em^2 - um - k)$$

$$\therefore m_1, m_2 = \frac{u \pm \sqrt{u^2 + 4kE}}{2E} = \frac{u}{2E} \left\{ 1 \pm \sqrt{1 + \frac{4kE}{u^2}} \right\}$$

$$\therefore \therefore C_1 = e^{m_1x} \text{ and } C_2 = e^{m_2x}$$

Let $\alpha = \sqrt{1 + \frac{4kE}{u^2}} > 1$, then $m_1, m_2 = \frac{u}{2E}(1 \pm \alpha)$

These functions are linearly independent and hence form a fundamental set of solution.

Therefore, general solution of the form of

$$C = K_1 \exp(m_1x) + K_2 \exp(m_2x)$$

K_1 and K_2 can be evaluated from B.C.'s.

Boundary conditions are

$$C = 0 \text{ at } x = \pm\infty$$

$$C = C_0 \text{ at } x = 0$$

For $x \leq 0$

$$C = 0 = K_1 e^{m_1(-\infty)} + K_2 e^{m_2(-\infty)} = K_1 e^{-\infty} + K_2 e^{+\infty} \rightarrow K_2 = 0$$

$$C = C_0 = K_1 + K_2 = K_1 \quad \therefore C_0 = K_1$$

For $x \geq 0$

$$C = 0 = K_1 e^{m_1 \infty} + K_2 e^{m_2 \infty} = K_1 e^{+\infty} + K_2 e^{-\infty} \rightarrow K_1 = 0$$

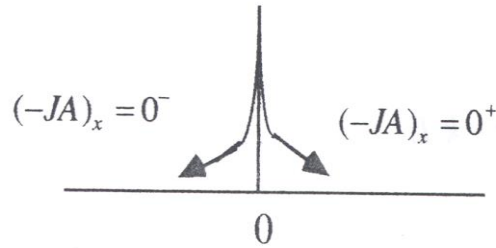
$$C = C_0 = K_1 + K_2 = K_2 \quad \therefore C_0 = K_2$$

Solutions are

$$C = C_0 e^{m_1 x}, \quad x \leq 0$$

$$C = C_0 e^{m_2 x}, \quad x \geq 0$$

To get C_0 , Consider flux



$$W = (-JA)_{x=0^-} + (-JA)_{x=0^+} = -\left(uC_0 - E \frac{\partial C}{\partial x} \Big|_{x=0^-}\right) A + \left(uC_0 - E \frac{\partial C}{\partial x} \Big|_{x=0^+}\right) A$$

$$\therefore \frac{W}{EA} = \left(\frac{\partial C}{\partial x}\right)_{x=0^-} - \left(\frac{\partial C}{\partial x}\right)_{x=0^+}$$

$$x \leq 0: \quad C = C_0 e^{m_1 x}$$

$$\frac{\partial C}{\partial x} = C_0 m_1 e^{m_1 x}; \quad \text{at } x = 0^-, \quad \frac{\partial C}{\partial x} = C_0 m_1$$

$$x \geq 0: C = C_0 e^{m_2 x}$$

$$\frac{\partial C}{\partial x} = C_0 m_2 e^{m_2 x}; \text{ at } x = 0^+, \frac{\partial C}{\partial x} = C_0 m_2$$

$$\therefore \frac{W}{EA} = C_0 m_1 - C_0 m_2 = C_0 (m_1 - m_2)$$

$$= C_0 \frac{u}{2E} (1 + \alpha - (1 - \alpha)) = C_0 \frac{u}{2E} [2\alpha] = C_0 \frac{u}{E} \alpha$$

$$C_0 = \frac{W}{uA} \frac{1}{\alpha} = \frac{W}{Q} \frac{1}{\alpha}$$

Note that

$$\text{If } k = 0 \text{ or } E = 0 \rightarrow C_0 = \frac{W}{Q}; \alpha = \sqrt{1 + \frac{4kE}{u^2}} = 1$$

• Comparison of initial mixing distance X_m with decay distance X_d

Initial mixing distance X_m for steady flow (state)

$$X_m = 0.4 \bar{u} W^2 / \varepsilon_t \quad \text{(a)}$$

Distance required for decay of substance to a factor of e^{-1} (0.3678)

$$X_d = \bar{u} / k \quad \text{(b)}$$

Therefore, ratio is given as

$$\frac{X_d}{X_m} = \frac{\bar{u} / k}{0.4 \bar{u} W^2 / \varepsilon_t} = 2.5 \frac{\varepsilon_t}{kW^2} \quad (c)$$

$$\text{Set } \alpha_1 = \frac{4Ek}{\bar{u}^2} \quad (d)$$

$$\text{Eq. (5.19): } E = 0.011 \bar{u}^2 W^2 / du^* \quad (e)$$

$$\text{Eq.(5.6): } \varepsilon_t = 0.6 du^* \quad (f)$$

Thus, combining these equations gives

$$\alpha_1 = 0.0264 W^2 k / \varepsilon_t \quad (g)$$

Equating (c) and (g) yields

$$\frac{X_d}{X_m} = \frac{0.06}{\alpha_1}$$

Consider analytical solution for non-conservative substance with dispersion and decay terms

$$\begin{aligned} C(x) &= C_0 \exp \left\{ -\frac{kx}{\bar{u}} \left[\frac{2}{\alpha_1} (\sqrt{\alpha_1 + 1} - 1) \right] \right\} \\ &= C_0 \exp \left\{ -\frac{\bar{u}x}{2E} (\sqrt{\alpha_1 + 1} - 1) \right\}, x \geq 0 \end{aligned} \quad (6.33)$$

If $\frac{X_d}{X_m} > 1$ ($X_d > X_m$)

Then,

$$\frac{0.06}{\alpha_1} > 1 \rightarrow \alpha_1 < 0.06 \rightarrow \left[\left(\frac{2}{\alpha_1} \right) (\sqrt{\alpha_1 + 1} - 1) \right] \approx 0.985 \approx 1$$

From Eq. (6.33), this means that

$$C \cong C_0 \exp \left\{ -\frac{kx}{\bar{u}} \right\} \rightarrow \text{solution for case w/o dispersion}$$

Therefore, there are two possibilities

(i) $X_d > X_m$

→ The longitudinal dispersion term has a negligible effect.

→ We may drop the dispersion term.

→ We may use an analytical solution. $C = C_0 \exp \left\{ -\frac{kx}{\bar{u}} \right\}$

(ii) $X_d < X_m$

→ The material decays before it mixes across the cross section

→ Eq. (6.32) is not a suitable model.

→ The concentration distribution must be computed numerically.

6.2.2 Time Variable Analysis

Time variable behavior of water quality in river downstream of an outfall to describe

- 1) the downstream transport of peak in a waste-water discharge load;
- 2) an accidental spill of a chemical;
- 3) the day-to-day variation in water quality due to day-to-day changes in waste load inputs.

◆ Three types

W/O Dispersion	W/ Dispersion	
	Instantaneous Input	Continuous Input
<ul style="list-style-type: none"> ▪ No mixing in the longitudinal direction ▪ Plug flow ▪ Impulse input remains its shape as it progress downstream 	<ul style="list-style-type: none"> ▪ Stream dispersion spreads the response temporally and spatially. ▪ used to estimate the transient effects due to inputs such as BOD from storm water overflow (by pass from combined sewer system) and batch discharges of municipal & industrial wastes 	<ul style="list-style-type: none"> ▪ Rectangular input ▪ $\eta = \frac{kE}{u^2} \rightarrow$ dimensionless ▪ Relative effects of longitudinal mixing for a nonconservative substance <ul style="list-style-type: none"> ① upland stream $\eta \approx < 0.01 \rightarrow$ not significant ② Main drainage rivers $\eta \approx 0.01 \sim 0.5 \rightarrow$ significant ③ Large rivers $\eta \approx 0.5 \sim 1.0$

Time variable equations & solutions

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

$$S = -kC \rightarrow \text{first-order decay}$$

Item	W/O Dispersion	W/ Dispersion	
G.E.	$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} - kC$	$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} + E \frac{\partial^2 C}{\partial x^2} - kC$	
Case	Case 5	Case 6	Case 7
B.C.'s	$C = (0) = C_0$ $C_0 = \frac{W(t)}{Q}$	Instantaneous Input	Continuous Input over an interval of time
		$M = M \delta(x)$	\pm Rectangular Input $C(x=0, t < \tau) = C_0$ $C(x=0, t > \tau) = 0$
Sol.	$C(x,t) = \frac{W(t-t^*) \exp\left(-\frac{kx}{u}\right)}{Q}$	$C(x,t) = \frac{M}{A\sqrt{4\pi Et}} \exp\left[\frac{-(x-ut)^2}{4Et} - kt\right]$ mean = ut variance $\sigma^2 = 4Et$	$C(x,t) = \frac{C_0}{2} \cdot \exp\left(-\frac{kx}{u}\right) \left[\operatorname{erf}\left(\frac{x-u(t-\tau)(1+\eta)}{\sqrt{4E(t-\tau)}}\right) - \operatorname{erf}\left(\frac{x-nt(1+\eta)}{\sqrt{4Et}}\right) \right]$ $\tau = \text{time interval of input}$ $\eta = \frac{kE}{u^2}$

6.3 Modeling BOD-DO Coupled System

6.3.1 Solutions of BOD-DO Coupled System

◆ Coupled system (BOD, DO)

- determination of dissolved oxygen concentrations downstream of a discharge of BOD

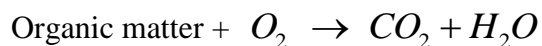
◆ Oxygen Demand

= indirect measure of organic materials (= organic pollutants) in terms of the amount of oxygen required to (completely) oxidize it.

COD - Chemical Oxygen Demand

BOD: CBOD - Carbonaceous BOD

 NBOD - Nitrogenous BOD



◆ Importance of dissolved oxygen (DO)

- Anaerobic conditions in a stream are indicative of extreme pollution

- Low dissolved oxygen concentrations have severe effects on the kind of biota which inhabit the stream

◆ Sources and sinks of DO

(a) Sources

- Reaeration from the atmosphere
- Photosynthetic oxygen production
- DO in incoming tributaries

(b) Sinks

- Oxidation of BOD
- Oxygen demand of sediments of water body
- Use of oxygen for respiration by aquatic plants

$$\therefore \frac{dC}{dt} = \text{reaeration} + (\text{Photosynthesis-respiration}) - \text{oxydation of BOD}$$

- sediment oxygen demand \pm oxygen transport (into and out of segment)

Let C = concentration of DO

L = concentration of BOD

(1) rate of utilization of DO by BOD

$$\frac{dL}{dt} = -k_1 L \rightarrow \text{exertion of BOD}$$

= utilization of DO

= depletion of DO

k_1 = deoxygenation coefficient

(2) reaeration from the atmosphere

= diffuse of oxygen into the stream rate of reaeration

\propto degree to which the water is unsaturated with oxygen

Let C_s = DO saturation concentration

then oxygen deficit, $DOD = C_s - C$

\therefore rate of reaeration

$$\frac{dC}{dt} = +k_2(C_s - C)$$

k_2 = reaeration coefficient (1/T)

\therefore Conservation equation for C

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} + E \frac{\partial^2 C}{\partial x^2} - k_1 L + k_2(C_s - C)$$

Let $D = C_s - C$

Then $dD = -dC$

$$\therefore -\frac{\partial D}{\partial t} = +u\frac{\partial D}{\partial x} - E\frac{\partial^2 D}{\partial x^2} - k_1L + k_2D$$

$$\frac{\partial D}{\partial t} = -u\frac{\partial D}{\partial x} + E\frac{\partial^2 D}{\partial x^2} + k_1L - k_2D \Rightarrow \text{G.E. for DO Deficit}$$

For BOD

$$\frac{\partial L}{\partial t} = -u\frac{\partial L}{\partial x} + E\frac{\partial^2 L}{\partial x^2} - k_1L \Rightarrow \text{G.E. for BOD concentration}$$

Let reaction terms

$$S_L = -k_rL$$

$$S_D = k_dL - k_aD$$

in which

L = concentration of remaining BOD

D = dissolved oxygen deficit (DOD) = $C_s - C$

C_s = DO saturation concentration

C = actual DO concentraion

k_r = BOD removal coefficient = $k_d + k_s$

k_s = settling coefficient

k_d = deoxygenation coefficient = biochemical degradation

k_a = reaeration coefficient

G.E.: unsteady state

$$\text{BOD } \frac{\partial L}{\partial t} = -u \frac{\partial L}{\partial x} + E \frac{\partial^2 L}{\partial x^2} - k_r L$$

$$\text{DOD } \frac{\partial D}{\partial t} = -u \frac{\partial D}{\partial x} + E \frac{\partial^2 D}{\partial x^2} + k_d L - k_a D$$

◆ Steady state, W/ Dispersion (Estuary)

(i) BOD: $0 = -u \frac{\partial L}{\partial x} + E \frac{\partial^2 L}{\partial x^2} - k_r L \rightarrow$ same as case 4

$$L = L_0 \exp\left[\frac{u}{2E}(1 + \alpha_r)x\right], \quad x \leq 0$$

$$= L_0 \exp\left[\frac{u}{2E}(1 - \alpha_r)x\right], \quad x \geq 0$$

in which

$$L_0 = \frac{W}{Q\alpha_r}$$

$$\alpha_r = \sqrt{1 + \frac{4k_r E}{u^2}}$$

(ii) DOD: $0 = -u \frac{\partial D}{\partial x} + E \frac{\partial^2 D}{\partial x^2} + k_d L - k_a D$

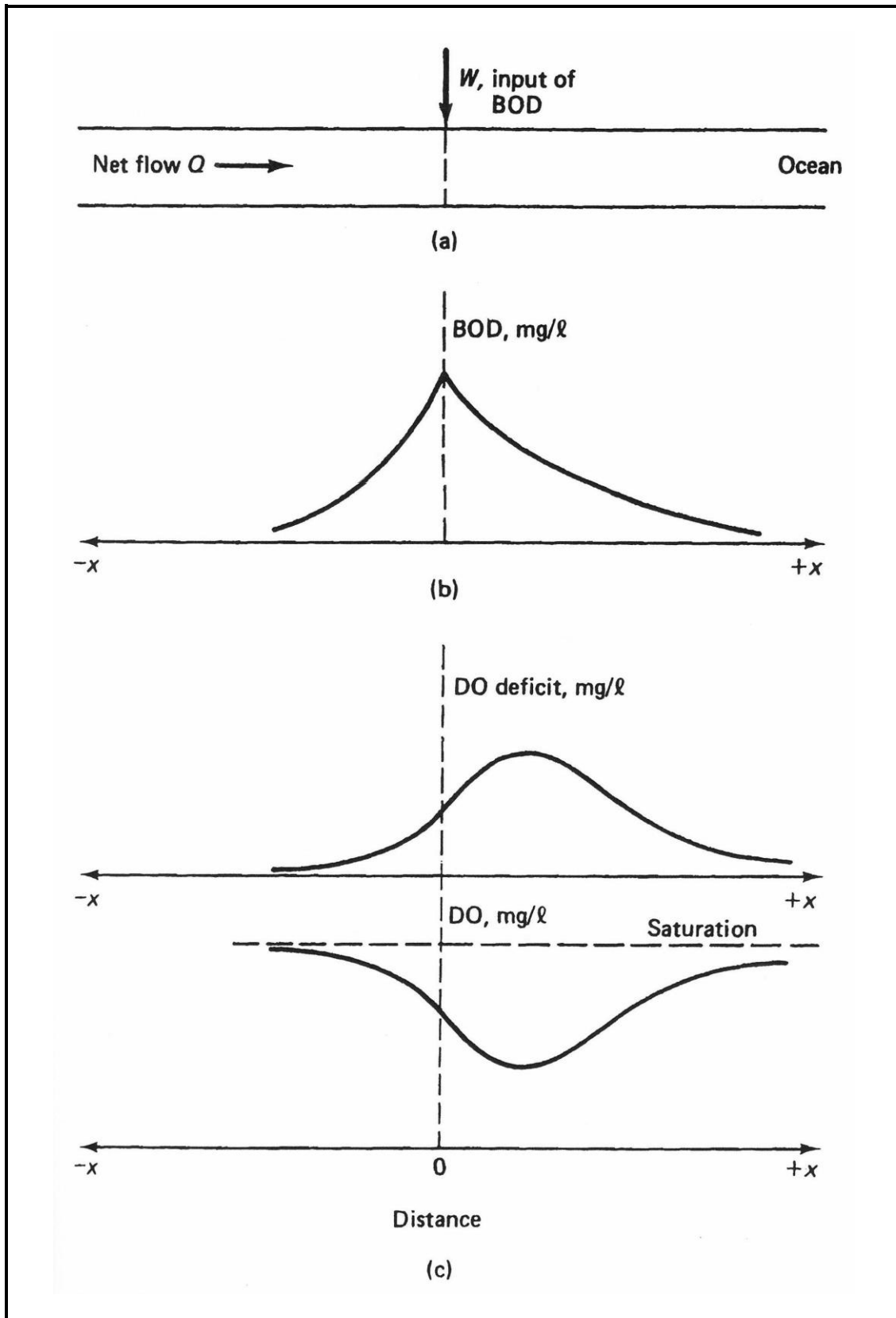
$$D = \frac{W}{Q} \frac{k_d}{k_a - k_r} \left\{ \frac{\exp\left[\frac{u}{2E}(1 + \alpha_r)x\right]}{\alpha_r} - \frac{\exp\left[\frac{u}{2E}(1 - \alpha_a)x\right]}{\alpha_a} \right\}, \quad x \leq 0$$

$$D = \frac{W}{Q} \frac{k_d}{k_a - k_r} \left\{ \frac{\exp\left[\frac{u}{2E}(1 - \alpha_r)x\right]}{\alpha_r} - \frac{\exp\left[\frac{u}{2E}(1 + \alpha_a)x\right]}{\alpha_a} \right\}, \quad x \geq 0$$

in which

$$\alpha_a = \sqrt{1 + \frac{4k_a E}{u^2}}$$

Thomann & Mueller (1987)



6.3.2 Streeter-Phelps Equation

◆ Streeter-Phelps Equation (1925)

- no dispersion (river) $E = 0$

- steady state

$$\text{BOD: } 0 = -u \frac{\partial L}{\partial x} - k_1 L$$

$$\text{DOD: } 0 = -u \frac{\partial D}{\partial x} + k_1 L - k_2 D$$

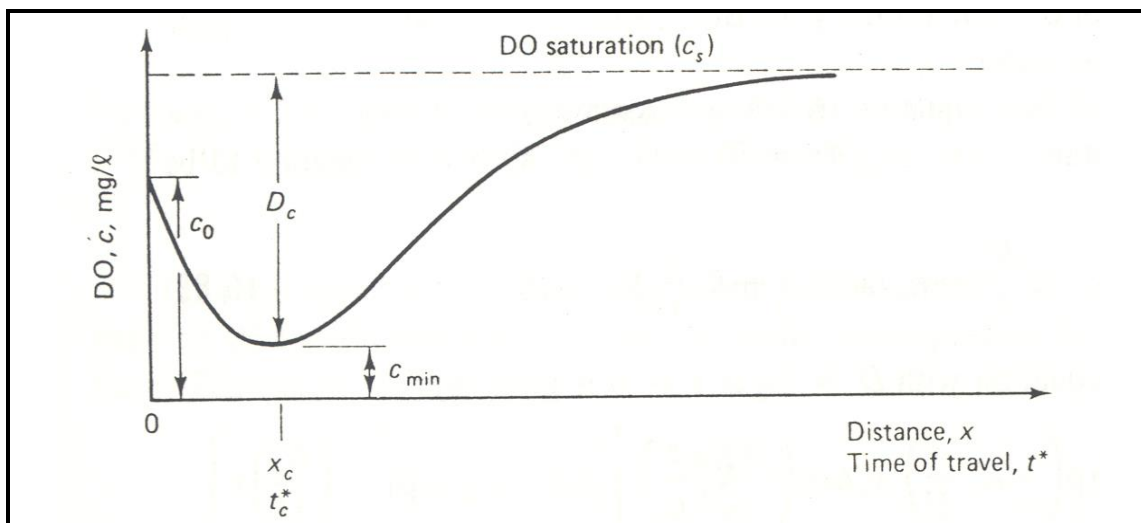
For BOD we have solution (Case 3)

$$\therefore L = L_0 \exp\left(-\frac{k_1}{u} x\right) = \frac{W}{Q} \exp\left(-\frac{k_1}{u} x\right)$$

B.C.: $D(0) = D_0 = C_s - C_0$

Solution:

$$D(x) = \frac{k_1}{k_2 - k_1} L_0 \left[e^{-\left(\frac{k_1}{u}\right)x} - e^{-\left(\frac{k_2}{u}\right)x} \right] + D_0 e^{-\left(\frac{k_2}{u}\right)x}, \quad x \geq 0 \quad (1)$$



- ◆ Critical deficit D_c (@ t_c uptake of oxygen by BOD is just balanced by the input of oxygen from atmosphere)

let $x/u = t$ (= time of flow) time of travel

→ Then Eq. (1) becomes

$$D(t) = \frac{k_1}{k_2 - k_1} L_0 [e^{-k_1 t} - e^{-k_2 t}] + D_0 e^{-k_2 t}, \quad x \geq 0 \quad (2)$$

→ t_c may be found as

$$\frac{\partial D}{\partial t} = 0; \quad t_c = \frac{1}{k_2 - k_1} \ln \left\{ \frac{k_2}{k_1} \left[1 - \frac{(k_2 - k_1) D_0}{k_1 L_0} \right] \right\}$$

$$D_c = \frac{k_1}{k_2} L_0 e^{-k_1 t_c} \quad \leftarrow \text{from Eq.(2)}$$

- ◆ Modified Streeter-Phelps equation

- account for other processes

(1) BOD removal due to sedimentation

- non-oxygen-demanding

- reduces BOD w/o changing oxygen concentration

$$\frac{\partial L}{\partial t} = -k_3 L$$

(2) BOD addition due to scour from the bottom and surface runoff from the land

- rate of addition is assumed to be constant

(3) Oxygen use other than by aerobic biochemical oxygen demand in the water, and oxygen addition other than through reaeration.

- net of these processes is constant rate A

◆ Solution :

$$D_t = \frac{k_1}{k_2 - (k_1 + k_3)} \left(L_0 - \frac{P}{k_1 + k_2} \right) \left\{ e^{-(k_1 + k_2)t} - e^{-k_2 t} \right\} + \frac{k_1}{k_2} \left(\frac{P}{k_1 + k_2} - \frac{A}{k_1} \right) (1 - e^{-k_2 t})$$

Consider only k_3 neglect A & P

Let $k_r = k_1 + k_3$, $k_d = k_1$, $k_s = k_3$, $k_a = k_2$

Then

$$D_t = \frac{k_d}{k_a - k_r} L_0 \left\{ e^{-k_r t} - e^{-k_a t} \right\} + D_0 e^{-k_a t}$$

[Remark]

$$\text{G.E.: } 0 = -u \frac{\partial L}{\partial x} - k_r L \quad \text{BOD}$$

$$0 = -u \frac{\partial D}{\partial x} + k_d L - k_a D \quad \text{DOD}$$