Urban Environmental Engineering 5

Taro Urase
Tokyo Institute of Technology

Lecture in the Last time

- Turbulent Diffusion
  - Time smoothing of diffusion equation
- Concentration (Mass density, ….)
- Exercise

Today's Lecture

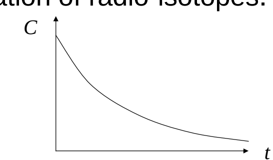
- Reaction Kinetics
  - First order reaction
  - Zero order reaction
  - Monod Equation
  - Streeter Phelps equation
  - First order reactions in series

First order reaction

- This type of reaction is often seen in environments. First order reaction is a reaction whose rate is in proportional to its concentration. One of the famous examples is deformation of radio-isotopes.

$$\frac{dC}{dt} = -k_1 C$$

$$C = C_0 \exp(-k_1 t)$$



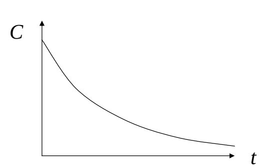
The concept of half life

- Half life time can be defined in the case of first order reaction.

$$t_{1/2} = \frac{1}{k_1} \ln 2$$

$$\frac{dC}{dt} = -k_1 C$$

$$C = C_0 \exp(-k_1 t)$$

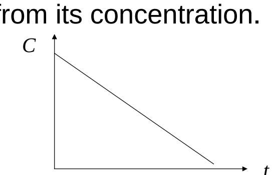


Zero order reaction

- This type of reaction is also seen in environments where the concentration of target compounds is not the limiting factor. Zero order reaction is a reaction whose rate is independent from its concentration.

$$\frac{dC}{dt} = -k_1$$

$$C = C_0 - k_1 t$$

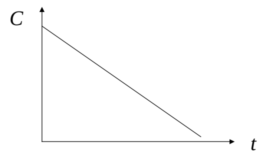


Half life time in zero order reaction

- Half life time concept is not frequently used in the case of zero order reaction, because half life time is dependent on initial concentration in the case of zero order reaction.

$$\frac{dC}{dt} = -k_1$$

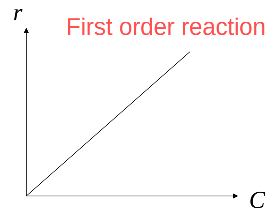
$$C = C_0 - k_1 t$$

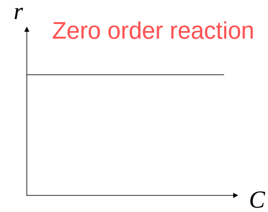


Reaction rate

- Reaction rate is defined as

$$r = -\frac{dC}{dt}$$

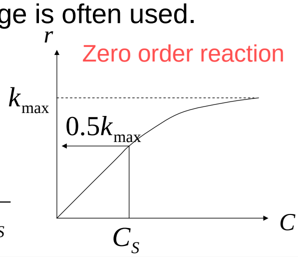




Monod-type rate constant

- Monod-type rate constant, which follow first order reaction in low concentration range and zero order reaction in high concentration range is often used.

$$r = -\frac{dC}{dt} = k_{\max}\frac{C}{C + C_S}$$



Growth of algae in lake and in sea

- The growth of phytoplankton is often modeled by using triple-monod-rate equation.

$$r = \frac{dX}{dt} = k_{\max}\frac{[N]}{[N] + C_{S,N}} \bullet \frac{[P]}{[P] + C_{S,P}} \bullet \frac{[I]}{[I] + C_{S,I}} X$$

X: Mass density of Phytoplankton

N: Nitrogen concentration

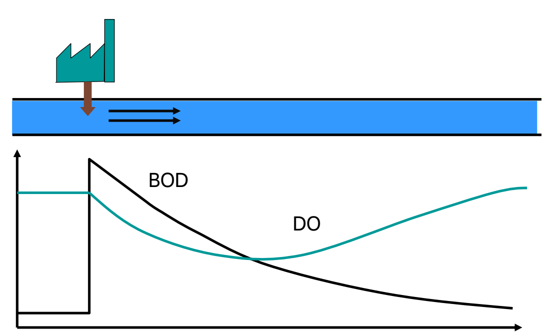
P: Phosphorous concentration

I : Irradiation

Streeter Phelps's Equation

- A set of differential equations describing changes in DO and BOD.
- This equation is used for assessing the point where minimum DO will be observed.

Change in DO and BOD



Streeter Phelps's equation

$$\frac{d[BOD]}{dt} = -k_1[BOD]$$

$$\frac{d[DO]}{dt} = -k_1[BOD] + k_2([DO]_{sat} - [DO])$$

Reduction of BOD and Consumption of DO

First order Reaction Constant

$$\frac{d[BOD]}{dt} = -k_1[BOD]$$

$$\frac{d[DO]}{dt} = -k_1[BOD] + k_2([DO]_{sat} - [DO])$$

DO recovery

$$\frac{d[BOD]}{dt} = -k_1[BOD]$$

$$\frac{d[DO]}{dt} = -k_1[BOD] + k_2([DO]_{sat} - [DO])$$

DO recovery constant

Saturated DO conc.

Reduction in BOD

$$\frac{d[BOD]}{dt} = -k_1[BOD]$$

is a first order linear differential equation and this can easily be solved into exponential form.

$$[BOD] = [BOD]_{t=0} \exp(-k_1 t)$$

Change in DO

$$\frac{d[DO]}{dt} = -k_1[BOD] + k_2([DO]_{sat} - [DO])$$

Here, we define y as $y=([DO]_{sat} - [DO])$.

$$\frac{dy}{dt} = -\frac{d[DO]}{dt}$$

$$\frac{dy}{dt} = k_1 L_0 \exp(-k_1 t) - k_2 y$$

where $L_0 = [BOD]_{t=0}$.

How can we solve the DO equation

$$\frac{dy}{dt} = k_1 L_0 \exp(-k_1 t) - k_2 y$$

We call this equation linear non-homogeneous first order differential equation. This equation can be solved by constant variation method.

How can we solve the DO equation

$$\frac{dy}{dt} = \boxed{k_1 L_0 \exp(-k_1 t)} - k_2 y$$

Non-homogeneous part

Homogeneous parts

We call this equation linear non-homogeneous first order differential equation. This equation can be solved by constant variation method.

Constant variation method

This type of differential equations has following solution.

$$y = C(t)\exp(-k_2 t)$$

By substituting this solution to the original differential equation, following equations will be obtained.

$$\frac{dy}{dt} = C(t)(-k_2)\exp(-k_2 t) + \frac{dC(t)}{dt}\exp(-k_2 t)$$
$$= k_1 L_0 \exp(-k_1 t) - k_2 C(t)\exp(-k_2 t)$$

Detailed modifications

$$\frac{dy}{dt} = \cancel{C(t)(-k_2)\exp(-k_2 t)} + \boxed{\frac{dC(t)}{dt}\exp(-k_2 t)}$$
$$= \boxed{k_1 L_0 \exp(-k_1 t)} - \cancel{k_2 C(t)\exp(-k_2 t)}$$

Focussing on $\boxed{} = \boxed{}$

$$\frac{dC(t)}{dt}\exp(-k_2 t) = k_1 L_0 \exp(-k_1 t)$$

Detailed modification (Contd.)

$$C(t) = \frac{k_1 L_0}{k_2 - k_1}\exp[(k_2 - k_1)t] + C_0$$

Integral constant

Going back to the oridinal equation, we obtain

$$y = \left(\frac{k_1 L_0}{k_2 - k_1}\exp[(k_2 - k_1)t] + C_0\right)\exp(-k_2 t)$$

Final solution which satisfies the initial condition

If we assume initial condition of $y=y_0$ at $t=0$,

$$y_0 = \frac{k_1 L_0}{k_2 - k_1} + C_0$$

By solving this equation for Co and by substituting this into the original equation, we obtain the final solution

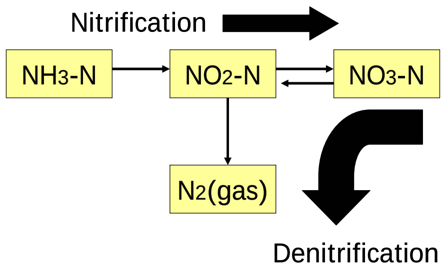
$$y = \frac{k_1 L_0}{k_2 - k_1}\left(\exp(-k_1 t) - \exp(-k_2 t)\right) + D_0 \exp(-k_2 t)$$

where D_0 is $DO_{sat}-[DO]_{t=0}$

Nitrogen

- TN (total nitrogen)
- DTN (Dissolved TN) and PTN (Particulate TN)
- NH3-N (Ammonia Nitrogen), NO2-N (Nitrite), NO3-N(Nitrate)

Nitrification and Denitrification



Nitrification takes place in the case of sufficient DO condition.

Denitrification takes place in the case of anoxic condition.

Equation of change in Nitrification

First order reactions in series

$$\frac{d[NH3-N]}{dt} = -k_1[NH3-N]$$

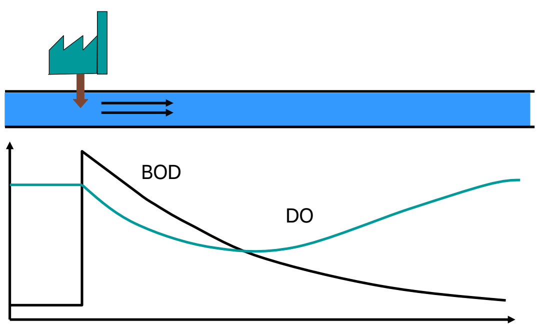
$$\frac{d[NO2-N]}{dt} = k_1[NH3-N] - k_2[NO2-N]$$

$$\frac{d[NO3-N]}{dt} = k_2[NO2-N]$$

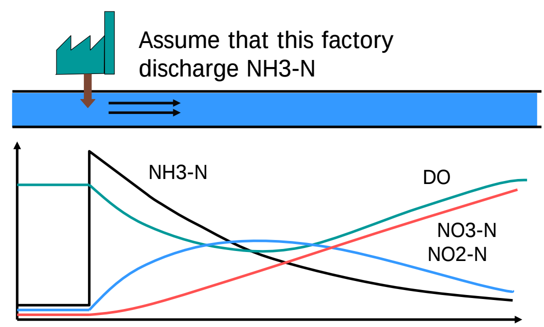
All Units are (mgN/L) or (mol/L)

If we use mgNH3/L, mgNO2/L, and mgNO3/L, the inclusion of conversion factor is necessary.

Change in DO and BOD



Change in Nitrogen



If DO is sufficient, NH_3-N is converted into NO_3-N

Nitrogen Removal Process using nitrification and denitrification