LESSON 13: DYNAMICS OF NON-CONSERVATIVE POLLUTANTS

NON CONSERVATIVE POLLUTANTS

Unlike the previous parts of the course, the transport of pollutants is <u>not conservative</u>. Some examples:

- **BOD** <u>Biological Oxygen Demand</u>. It is strictly related to the amount of biodegradable organic material. It is used to quantify the consumed oxygen by reactions

$$\underbrace{CH_2O}_{BOD} + \underbrace{O_2}_{DO} \xrightarrow{bacteria} CO_2 + H_2O$$

$$DO \rightarrow \textit{Dissolved Oxygen} \begin{cases} DO > 4.0\ \mathrm{mg/l} & \textit{Always} \\ DO \geq 5.0\ \mathrm{mg/l} & \textit{Averaged value} \end{cases}$$

- **NBOD** <u>Nitrogenous Biological Oxygen Demand</u>. It is related to ammonium nitrogen, which is toxic for almost the total organisms

$$\underbrace{NH_3}_{Ammonia} + 2O_2 \xrightarrow{bacteria} \underbrace{NO_3^-}_{Nitrate} + H_2O + \underbrace{H^+}_{Proton}$$

NON CONSERVATIVE POLLUTANTS

The equilibrium of the reaction in the water bodies is:

$$NH_3 + H^+ \longleftrightarrow \underbrace{NH_4^+}_{\textit{Ammonium ion}}$$

When $NH_3 + H^+ < NH_4^+$, then $pH = 6 \div 9$.
The water quality standard prescribes:

$$\underbrace{NH_3 - N}_{\textit{Ammonia Nitrogen}} + \underbrace{NH_4^+ - N}_{\textit{Ammonium Nitrogen}} < 2\ mg/l$$

- **TSS** <u>Total Suspended Solids</u>. They reduce the DO, cause of the oxidation occurring when the particles settle down on the bottom. Moreover they reduce the light penetration and in general they are togheter with Pathogens and Heavy Metals.

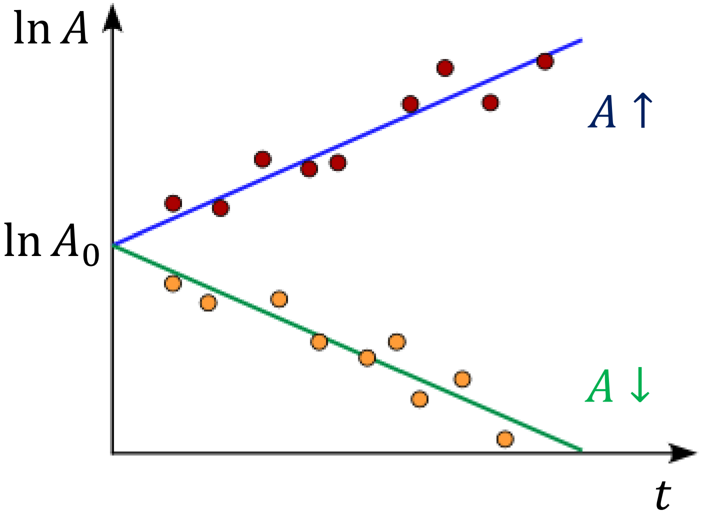
- **Coliform Bacteria**. They are index of water quality being the pathogen in water related with.

All these processes can be modeled by <u>first order reactions</u>.

FIRST ORDER REACTION

i. $A \xrightarrow{r} B$

$$\begin{cases} \dfrac{\mathrm{d}A}{\mathrm{d}t} = -rA \\ \dfrac{\mathrm{d}A}{\mathrm{d}t} = +rA \end{cases} \longrightarrow \begin{cases} A = A_0\, e^{-rt} \\ A = A_0\, e^{+rt} \end{cases}$$



Let's focus now on the product of the reaction B. The mass has to be conserved, i.e. the process is reversible

$$\begin{cases} \dfrac{\mathrm{d}B}{\mathrm{d}t} = +rA = rA_0\, e^{-rt} \\ \dfrac{\mathrm{d}B}{\mathrm{d}t} = -rA = -rA_0\, e^{rt} \end{cases}$$

$\longleftarrow$ When A decays, B is produced

$\longleftarrow$ When A is produced, B decays

Let's see the solution:

$$\mathrm{d}B = rA_0\, e^{-rt}\mathrm{d}t \xrightarrow{\int} B = -A_0\, e^{-rt} + c$$

FIRST ORDER REACTION

When $t = 0$: $\begin{cases} B = B_0 \\ A = A_0 \end{cases} \longrightarrow c = A_0 + B_0$ *Total mass involved in the reaction*

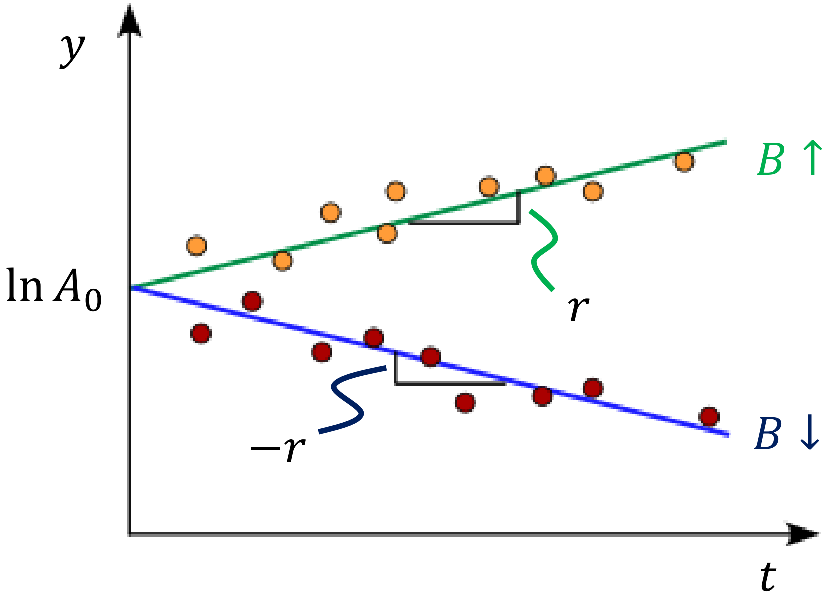
Then, we have: $\begin{cases} B = B_0 + A_0(1 - e^{-rt}) & A \downarrow \quad B \uparrow \\ B = B_0 + A_0(1 - e^{+rt}) & A \uparrow \quad B \downarrow \end{cases}$

In this case we can estimate the reaction speed r as following:

$$B - B_0 - A_0 = -A_0\, e^{\mp rt}$$

$$(B_0 + A_0) - B = A_0\, e^{\mp rt}$$

$$\underbrace{\ln[(B_0 + A_0) - B]}_{y} = \underbrace{\ln A_0}_{q} \underbrace{\mp rt}_{mt}$$



FIRST ORDER REACTION

ii. $A \xrightarrow{r} 2A$ *Cell growth*

The equation governing the process is:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = rA = rA_0\, e^{rt}$$

By separating the variables:

$$\mathrm{d}A = rA_0\, e^{rt}\mathrm{d}t \quad \xrightarrow{\int} \quad A = A_0\, e^{rt} + c$$

When $t = 0$: $A_0 = A_0 + c$ $\longrightarrow$ $c = 0$

Finally:

$$\longrightarrow \quad A = A_0\, e^{rt}$$

It is valid only in the first stage of growth

REACTION SPEED

In the first order reaction $r\ [s^{-1}]$.

It can be estimated by experimental analysis as: $r = \alpha e^{-\frac{E_a}{R\vartheta}}$

Where: α is a constant depending on the reaction

E_a [J mol^{-1}] is the energy starting the reaction up

$R = 8.314$ [J mol^{-1} K^{-1}] is the gas constant

ϑ [K] absolute temperature

It is important in our application the dependency of r with temperatures ϑ [K] or T [°C]:

$$\begin{cases} r_{\vartheta_1} = \alpha e^{-\frac{E_a}{R\vartheta_1}} \\ r_{\vartheta_2} = \alpha e^{-\frac{E_a}{R\vartheta_2}} \end{cases} \longrightarrow \frac{r_{\vartheta_1}}{r_{\vartheta_2}} = e^{-\frac{E_a}{R}\left(\frac{\vartheta_1-\vartheta_2}{\vartheta_1\vartheta_2}\right)}$$

In the water bodies T ranges between $0 \div 35$ °C. Hence, using the absolute temperatures:

$$\frac{E_a}{R}\frac{1}{\vartheta_1\vartheta_2} \cong \mathrm{const} \longrightarrow \frac{r_{\vartheta_1}}{r_{\vartheta_2}} = e^{-\mathrm{const}\ (\vartheta_1-\vartheta_2)}$$

It is importamt the difference between temperatures. We can use T *insted of* ϑ*.*

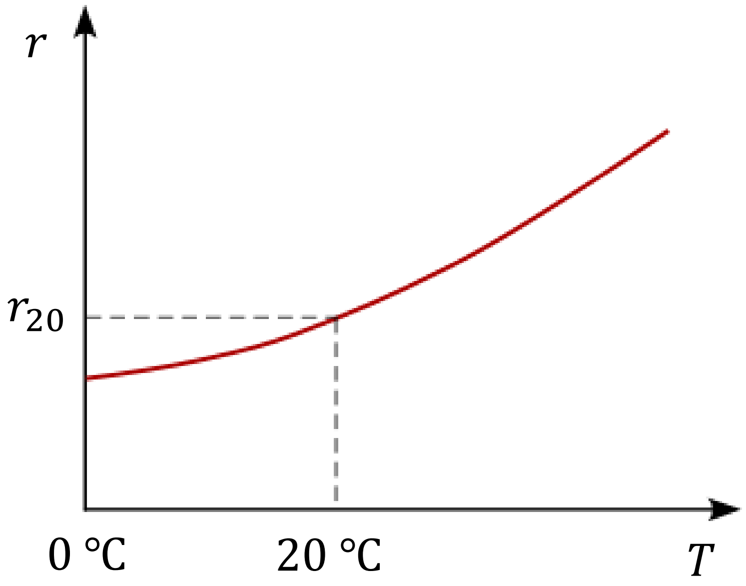
REACTION SPEED

The reaction speed r for a given T in the range between $0 \div 35$ °C can be approximated as:

$$r = r_{20}\beta^{T-20}$$

Where: r_{20} is the reaction speed of the process at 20 °C
β is a parameter depending by the process

Process	β
BOD	1.047
Aeration	1.024÷1.037
Algae photosynthesis	1.065
Nitrification	1.04
Bacteria respiration	1.03
Zooplankton respiration	1.06



TRANSPORT AND REACTION EQUATION

To study the problem analytically we should use the 1D approach. In this case the solute concentration C which reacts during the transport in water is described by:

$$\frac{\partial C}{\partial t}+\frac{Q}{A}\frac{\partial C}{\partial x}=K_x\frac{\partial^2 C}{\partial x^2}\mp rC$$

An analytical solution of this equation exists, albeit rather complex. However, under some assumptions and conditions, the equation can be simplified and the analytical solution, as well. For this aim, we use the following non-dimensional parameters:

- $Pe=\frac{UL}{K_x}=\frac{L^2}{K_x}\frac{U}{L}=\frac{T_d}{T_a}$ $\longrightarrow$ Peclet number: ratio between timescale of dispersion T_d and timescale of advection T_a
- $N_r=\frac{K_x r}{U^2}=r\frac{(L/U)^2}{L^2/K_x}=\frac{{T_a}^2}{T_r T_d}$ $\longrightarrow$ Reaction number: ratio between ${T_a}^2$ and timescale T_d per the timescale of reaction T_r

The Transport-Reaction Equation can be simplified when diffusion does not influence the process, i.e.:

$$\begin{cases} Pe \gg 1 \\ N_r \ll 1 \end{cases} \longrightarrow \frac{\partial C}{\partial t}+U\frac{\partial C}{\partial x}=\mp rC$$

We can solve it analytically!

CONVECTION AND REACTION EQUATION

The problem is described by the following system:

$$\begin{cases} \dfrac{\partial C}{\partial t} + U\dfrac{\partial C}{\partial x} = \mp rC \\ C(0,t) = C_0 \end{cases}$$

To solve it we need of changing the reference system, i.e. the observer moves with the mean flow velocity U:

$$C(x,t) \longrightarrow C(\xi,t) \qquad \text{with} \qquad \xi = x - Ut$$

As we have seen previously during the course, the problem in the new reference system can be rearranged in the following:

$$\begin{cases} \dfrac{\partial C}{\partial t} \pm rC = 0 \\ C(-\xi/U) = C_0 \end{cases}$$

By separating the variables, the first equation yields:

$$\frac{\mathrm{d}C}{C} = \mp r\mathrm{d}t \quad \xrightarrow{\int} \quad \ln C = \mp rt + a$$

CONVECTION AND REACTION EQUATION

For the Boundary Condition:

$$\ln C_0 = \pm r\frac{\xi}{U} + a \longrightarrow a = \ln C_0 \mp r\frac{\xi}{U}$$

Then, by replacing a:

$$\ln C = \mp rt + \ln C_0 \mp r\frac{\xi}{U}$$

$$\ln C - \ln C_0 = \mp r\left(t + \frac{\xi}{U}\right)$$

$$\ln\frac{C}{C_0} = \mp r\left(t + \frac{\xi}{U}\right) \xrightarrow{e} C = C_0 e^{\mp r\left(t+\frac{\xi}{U}\right)}$$

Moreover:

$$x = \xi + Ut \longrightarrow \frac{x}{U} = t + \frac{\xi}{U}$$

CONVECTION AND REACTION EQUATION

Finally:

$$\begin{cases} C = C_0 e^{-r\frac{x}{U}} & \longrightarrow \text{ solute mass decay} \\ C = C_0 e^{+r\frac{x}{U}} & \longrightarrow \text{ solute mass growth} \end{cases}$$

In these solutions r/U is the reference length. For the decay process:

$r\dfrac{x}{U}$	0	1	2	3
$\dfrac{C}{C_0}$	1	0.368	0.135	0.05

At 3 lengths scale the initial concentration is the 95% reduced!

It is worth noting that this solution assumes Uniform Flow. In the real case $U = U(x, t)$, thus the reference system has to move in according to:

$$\xi(x, t) = \frac{1}{A_0}\int_0^x A\,\mathrm{d}x' = U_0\int_0^x \frac{1}{U}\mathrm{d}x'$$

with A_0 and U_0 the values in $x = 0$.

Please note that in this case also $r = r(x, t)$.

THE STREETER-PHELPS EQUATION

It is the first model in order to study the presence of Biodegradable Organic Material into a watercourse and its effects on the DO which is reduced cause of the Biological Oxygen Demand.

Let's define:
- B BOD concentration $[kg/m^3]$
- O DO concentration $[kg/m^3]$
- O_s Saturate concetration of DO $[kg/m^3]$
- $\tilde{O} = O_s - O$ Deficit of DO $[kg/m^3]$
- r_d Deoxygenation rate $[s^{-1}]$
- r_a Aeration rate $[s^{-1}]$

The mass conservation and the reaction process of BOD give the following equation system. The work hypotheses are uniform flow and negligible dispersion process.

$$\begin{cases} \dfrac{\partial B}{\partial t} + U\dfrac{\partial B}{\partial x} = -r_d B & \longrightarrow \\ \dfrac{\partial O}{\partial t} + U\dfrac{\partial O}{\partial x} = -r_d B + r_a \tilde{O} & \longrightarrow \\ \dfrac{\partial \tilde{O}}{\partial t} + U\dfrac{\partial \tilde{O}}{\partial x} = r_d B - r_a \tilde{O} & \longrightarrow \end{cases}$$

BOD reduction.

DO evolution considering O_2 decay and production due to BOD redox and Aeration.

Deficit of DO evolution . It is complementary to DO.

THE STREETER-PHELPS EQUATION

The analytical solution is easily determined by assuming stationarity, i.e.:

$$\begin{cases} U\dfrac{\mathrm{d}B}{\mathrm{d}x} = -r_d B & \textcircled{1} \\ U\dfrac{\mathrm{d}O}{\mathrm{d}x} = -r_d B + r_a \tilde{O} & \textcircled{2} \\ U\dfrac{\mathrm{d}\tilde{O}}{\mathrm{d}x} = r_d B - r_a \tilde{O} & \textcircled{3} \end{cases}$$

The solution of (1) is: $B = B_0 e^{-r_d \frac{x}{U}}$

Whereas, focusing on (3) the equation can be rearranged as following:

$$\begin{cases} \dfrac{\mathrm{d}\tilde{O}}{\mathrm{d}x} + p\tilde{O} = q \\ \tilde{O}(0,0) = \tilde{O}_0 \end{cases}$$

In this case

$$p = r_a / U$$

$$q = \frac{r_d B}{U} = \frac{r_d B_0}{U} e^{-r_d \frac{x}{U}}$$

The solution of the system holds:

$$\tilde{O} = \tilde{O}_0 e^{-\gamma} + e^{-\gamma} \int_0^x e^{\gamma} q \, \mathrm{d}\xi$$

with

$$\gamma = \int_0^x p \, \mathrm{d}\xi = \frac{r_a x}{U}$$

THE STREETER-PHELPS EQUATION

By replacing the definition of γ and q, the equation reads:

$$\tilde{O} = \tilde{O}_0 e^{-\frac{r_a x}{U}} + e^{-\frac{r_a x}{U}} \int_0^x \frac{r_d B_0}{U} e^{-r_d \frac{\xi}{U}} e^{r_a \frac{\xi}{U}} \, \mathrm{d}\xi$$

$$\tilde{O} = \tilde{O}_0 e^{-\frac{r_a x}{U}} + \frac{r_d B_0}{U} e^{-\frac{r_a x}{U}} \int_0^x e^{(r_a - r_d)\frac{\xi}{U}} \, \mathrm{d}\xi$$

$$\int_a^b e^{f(x)} \, \mathrm{d}x = \frac{\left[e^{f(x)}\right]_a^b}{f'(x)}$$

$$\tilde{O} = \tilde{O}_0 e^{-\frac{r_a x}{U}} + \frac{r_d B_0}{\cancel{U}} e^{-\frac{r_a x}{U}} \frac{\cancel{U}}{r_a - r_d} \left[e^{(r_a - r_d)\frac{\xi}{U}}\right]_0^x$$

$$\tilde{O} = \tilde{O}_0 e^{-\frac{r_a x}{U}} + \frac{r_d B_0}{r_a - r_d} e^{-\frac{r_a x}{U}} \left[e^{(r_a - r_d)\frac{x}{U}} - 1\right]$$

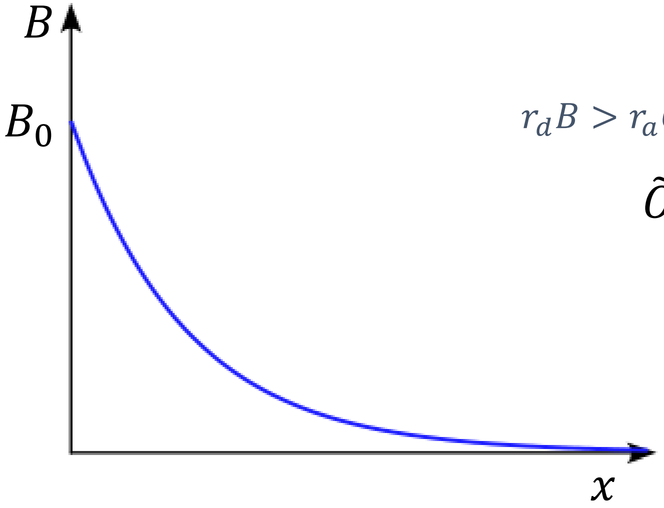
$$\longrightarrow \qquad \tilde{O} = \tilde{O}_0 e^{-r_a \frac{x}{U}} + B_0 \frac{r_d}{r_a - r_d} \left[e^{-r_d \frac{x}{U}} - e^{-r_a \frac{x}{U}}\right]$$

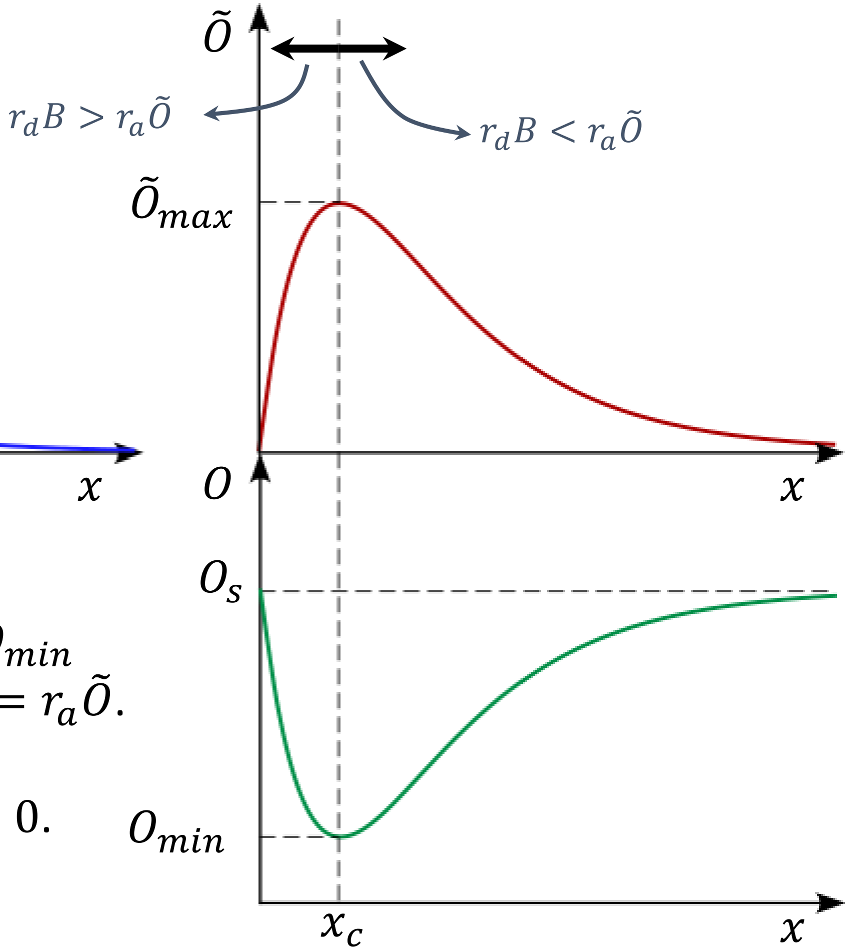
When $\tilde{O}_0 = 0$, it is simplified in: $\tilde{O} = B_0 \frac{r_d}{r_a - r_d} \left[e^{-r_d \frac{x}{U}} - e^{-r_a \frac{x}{U}}\right]$

THE STREETER-PHELPS EQUATION

The DO is then:

$$O = O_s - \tilde{O} = O_s - \overbrace{(O_s - O_0)}^{\tilde{O}_0} e^{-r_a \frac{x}{U}} - B_0 \frac{r_d}{r_a - r_d}\left[e^{-r_d \frac{x}{U}} - e^{-r_a \frac{x}{U}}\right]$$





x_c is the Critic Distance, where O_{min} (and $\tilde{O}_{max}$). In this section: $r_d B = r_a \tilde{O}$.

N.B. The initial condition is $\tilde{O}_0 = 0$.

THE CRITIC CONDITION

Let’s analyze the DO in x_c. $\tilde{O}_{max}$ (or O_{min}) means $\mathrm{d}\tilde{O}/\mathrm{d}x = 0$ (or $\mathrm{d}O/\mathrm{d}x = 0$), i.e.:

$$\frac{\mathrm{d}\tilde{O}}{\mathrm{d}x} + p\tilde{O} = q \quad \xrightarrow{\mathrm{d}\tilde{O}/\mathrm{d}x=0} \quad p\tilde{O} = q$$

That is: $\dfrac{r_a\tilde{O}_c}{U} = \dfrac{r_d B_0}{U} e^{-r_d\frac{x_c}{U}} \longrightarrow \tilde{O}_c = \dfrac{r_d}{r_a} B_0 e^{-r_d\frac{x_c}{U}}$

We can determine x_c by replacing $\tilde{O}_c$ into the analytical solution of $\tilde{O}$ in $x = x_c$. We find:

$$\frac{r_d}{r_a}\cancel{B_0} e^{-r_d\frac{x_c}{U}} = \frac{\tilde{O}_0}{B_0} e^{-r_a\frac{x_c}{U}} + \cancel{B_0}\frac{r_d}{r_a - r_d}\left[e^{-r_d\frac{x_c}{U}} - e^{-r_a\frac{x_c}{U}}\right]$$

$$\left(\frac{r_d}{r_a} - \frac{r_d}{r_a - r_d}\right) e^{-r_d\frac{x_c}{U}} = \left(\frac{\tilde{O}_0}{B_0} - \frac{r_d}{r_a - r_d}\right) e^{-r_a\frac{x_c}{U}}$$

$$\left[\frac{r_d\cancel{r_a} - r_d^{\,2} - r_d\cancel{r_a}}{r_a(r_a - r_d)}\right] e^{-r_d\frac{x_c}{U}} = \left[\frac{(r_a - r_d)\tilde{O}_0 - r_d B_0}{B_0(r_a - r_d)}\right] e^{-r_a\frac{x_c}{U}}$$

THE CRITIC CONDITION

By grouping the terms with the exponent the equation holds:

$$e^{(r_a-r_d)\frac{x_c}{U}} = -\left[\frac{r_a\cancel{(r_a-r_d)}}{{r_d}^2}\right]\left[\frac{(r_a-r_d)\tilde{O}_0 - r_d B_0}{B_0\cancel{(r_a-r_d)}}\right] = \frac{r_a r_d B_0 - r_a(r_a-r_d)\tilde{O}_0}{{r_d}^2 B_0}$$

$$e^{(r_a-r_d)\frac{x_c}{U}} = \frac{r_a}{r_d} - \frac{r_a}{r_d}\frac{r_a-r_d}{r_d}\frac{\tilde{O}_0}{B_0} = \frac{r_a}{r_d}\left(1-\frac{r_a-r_d}{r_d}\frac{\tilde{O}_0}{B_0}\right)$$

ln

$$(r_a-r_d)\frac{x_c}{U} = \ln\left[\frac{r_a}{r_d}\left(1-\frac{r_a-r_d}{r_d}\frac{\tilde{O}_0}{B_0}\right)\right]$$

$$\longrightarrow \quad x_c = \frac{U}{r_a-r_d}\ln\left[\frac{r_a}{r_d}\left(1-\frac{r_a-r_d}{r_d}\frac{\tilde{O}_0}{B_0}\right)\right]$$

When initially DO is assumed being in saturated condition, i.e. $\tilde{O}_0 = 0$:

$$\longrightarrow \quad x_c = \frac{U}{r_a-r_d}\ln\left(\frac{r_a}{r_d}\right)$$

PURIFICATION COEFFICIENT

For the Streeter-Phelps model the critic codition is equal to:

$$x_c = \frac{U}{r_a - r_d} \ln\left[\frac{r_a}{r_d}\left(1 - \frac{r_a - r_d}{r_d}\frac{\tilde{O}_0}{B_0}\right)\right] \qquad \tilde{O}_c = \frac{r_d}{r_a} B_0 e^{-r_d \frac{x_c}{U}}$$

It is worth noting that:

- $x_c \propto r_a / r_d$ → <u>Purification Coefficient</u>
- $\tilde{O}_c \propto (r_a/r_d)^{-1}$
- $\tilde{O}_c \propto B_0$

Generally, The value of x_c and $\tilde{O}_c$ depends on other parameters. In particular:

i. Temperature T

ii. Flow rate Q

iii. Initial Deficit of Oxygen $\tilde{O}_0$

ROLE OF TEMPERATURE

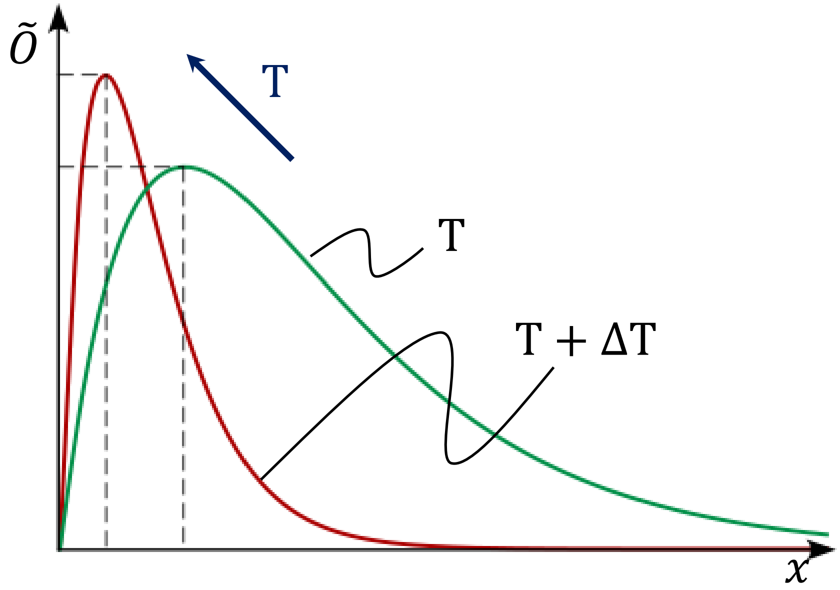
As we have seen: $\mathrm{T}\uparrow \longrightarrow r\uparrow$

In this case:

$$\begin{cases} r_a = r_{a,20} 1.024^{T-20} \\ r_d = r_{d,20} 1.048^{T-20} \end{cases} \longrightarrow \frac{r_a}{r_d}\downarrow \qquad \text{when T}\uparrow$$

Moreover the amount of oxygen to saturate water is smaller when T increasing, i.e.:

$$\mathrm{T}\uparrow \longrightarrow O_s\downarrow$$



The overall effect is:

$$\mathrm{T}\uparrow \longrightarrow \begin{matrix} \tilde{O}_c\uparrow \\ x_c\downarrow \end{matrix}$$

ROLE OF FLOW RATE

When Q increases:

- Initial BOD decreases ($B_0 \downarrow$) because the mass of BOD is constant, but the mass of water is greater.

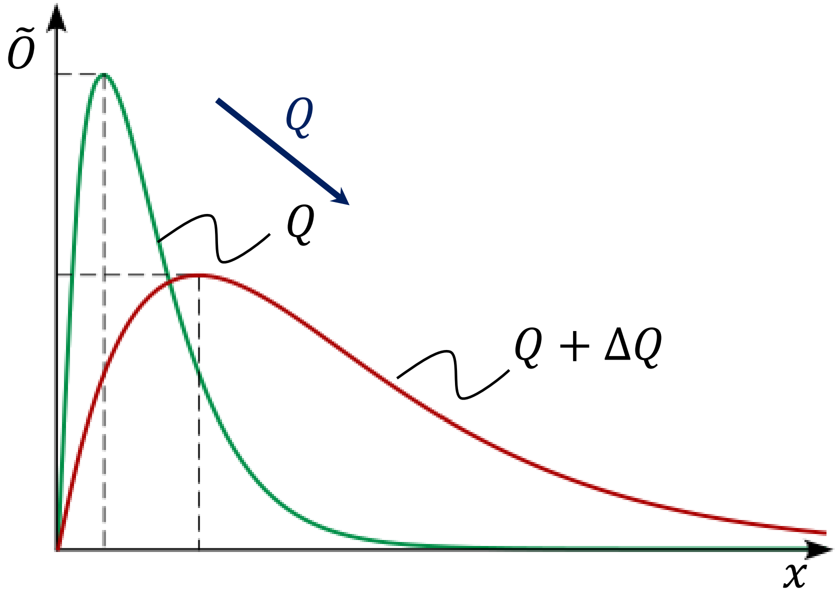
- Aeration r_a is affected in two counterposed ways:
  - $Q \uparrow \longrightarrow U \uparrow$ Higher U promotes the entrapment of air in the water
  - $Q \uparrow \longrightarrow z_0 \uparrow$ Higher z_0 means lower aeration because the exchange of air occurs only in the outer layer of water

$$\longrightarrow \quad r_a \propto \frac{U^m}{{z_0}^n} \quad m < 1, n > 1$$

The overall effect is: $Q \uparrow \longrightarrow r_a \downarrow$

By summarizing:

$$Q \uparrow \longrightarrow \begin{matrix} \tilde{O}_c \downarrow \\ x_c \uparrow \end{matrix}$$



ROLE OF INITIAL DEFICIT OF OXYGEN

When $\tilde{O}_0$ increases:

- $\tilde{O}_0 \uparrow \longrightarrow x_c \downarrow$ By the expression of x_c
- $\tilde{O}_0 \uparrow \longrightarrow \tilde{O}_c \uparrow$ Because the critic deficit of oxygen is inversely related by the critic distance x_c