CE 435 (January 2018 Semester)

Environmental Pollution and Management: Water Pollution

CN-3: Fate of Oxygen Demanding Wastes

Dr. M. Ashraf Ali
Professor of Civil Engineering, BUET

Fate of oxygen-demanding wastes

Microorganisms (Organic matter) + O_2 □ CO_2 + H_2O + New cells+
+Stable products

The actual BOD < the theoretical BOD due to incorporation of some carbon into bacterial cells

↓

Limited usefulness for practical purpose

BOD is an important metric to evaluate the effect of oxygen demanding wastes on streams and rivers

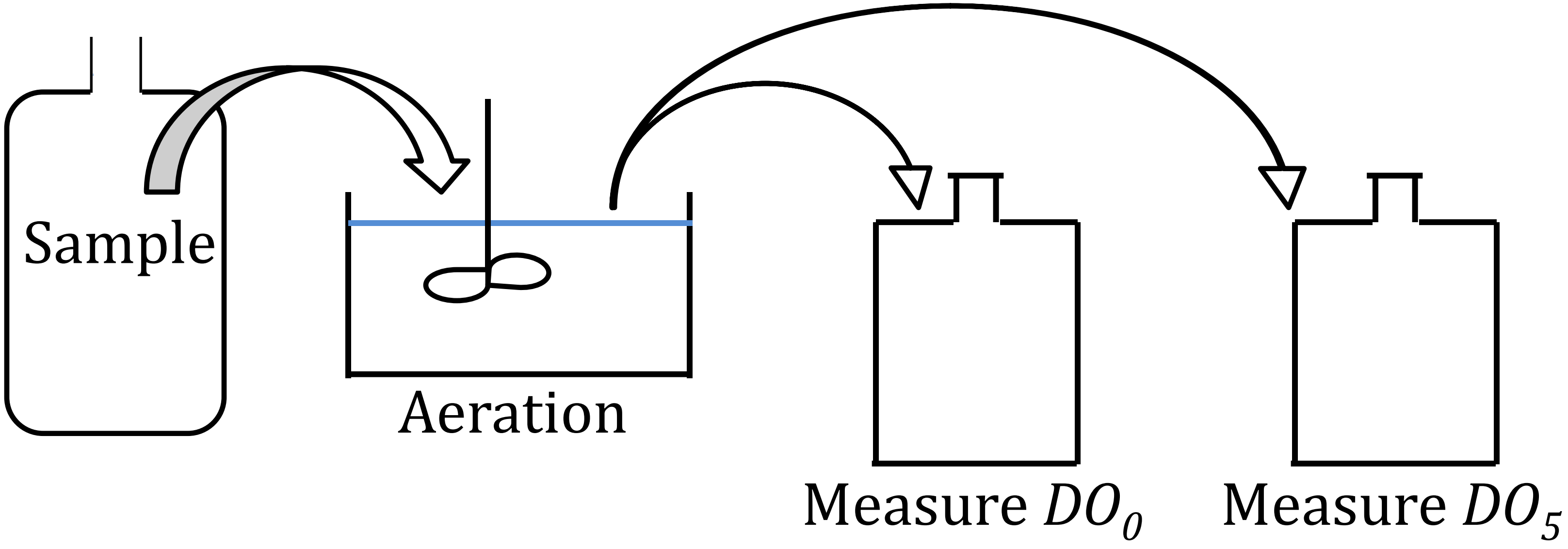
↓

Standard practice: **the 5-day BOD test (BOD$_5$)**

Laboratory measurement of BOD_5

Bottles specifically designed for incubation of water samples for BOD analysis.

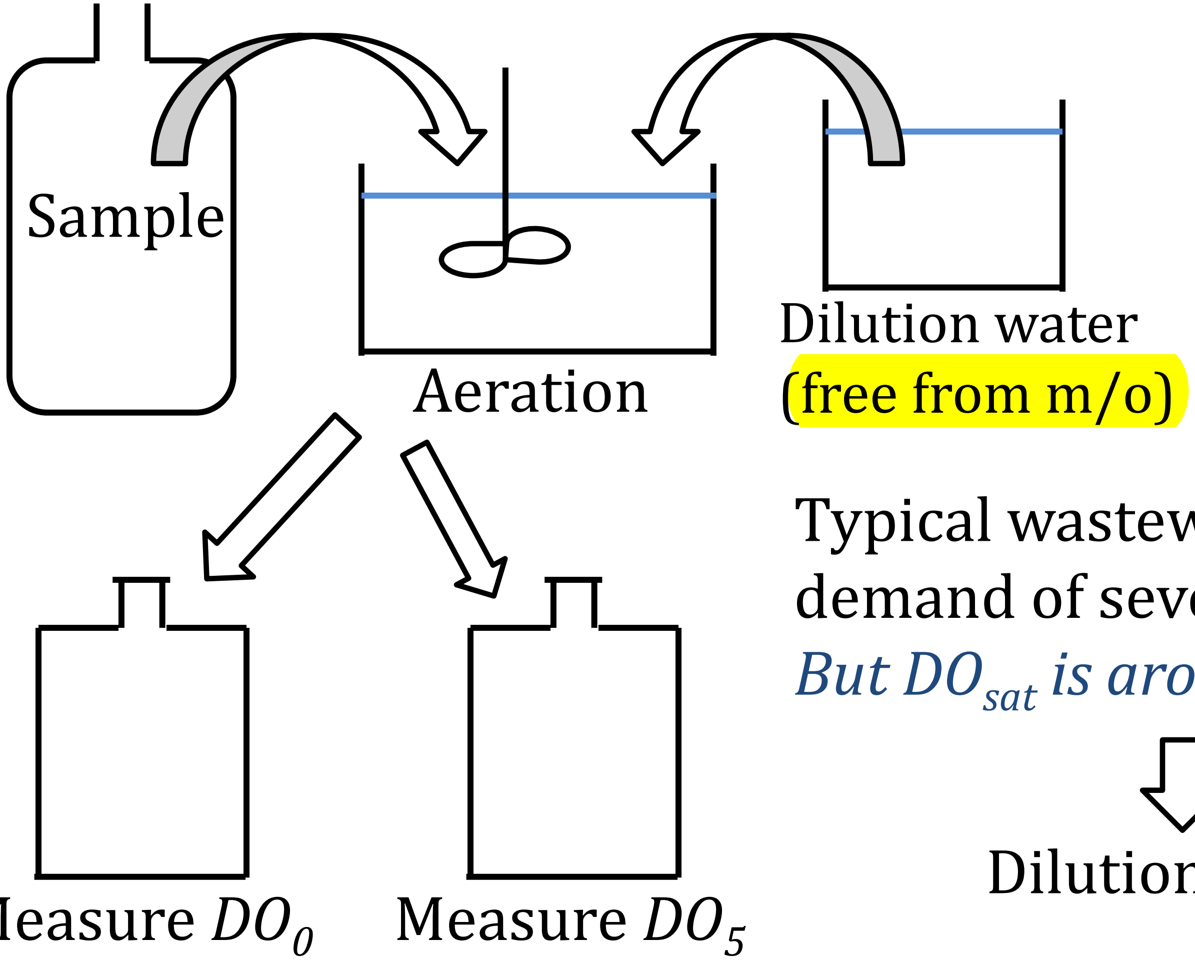
$$\boxed{BOD_5 = DO_0 - DO_5}$$



Laboratory measurement of BOD_5

With dilution

$$\boxed{BOD_5 = (DO_0 - DO_5) \times Dilution\ factor}$$



Typical wastewater has oxygen demand of several hundred mg/L

But DO_{sat} is around 9.1 mg/L

⇩

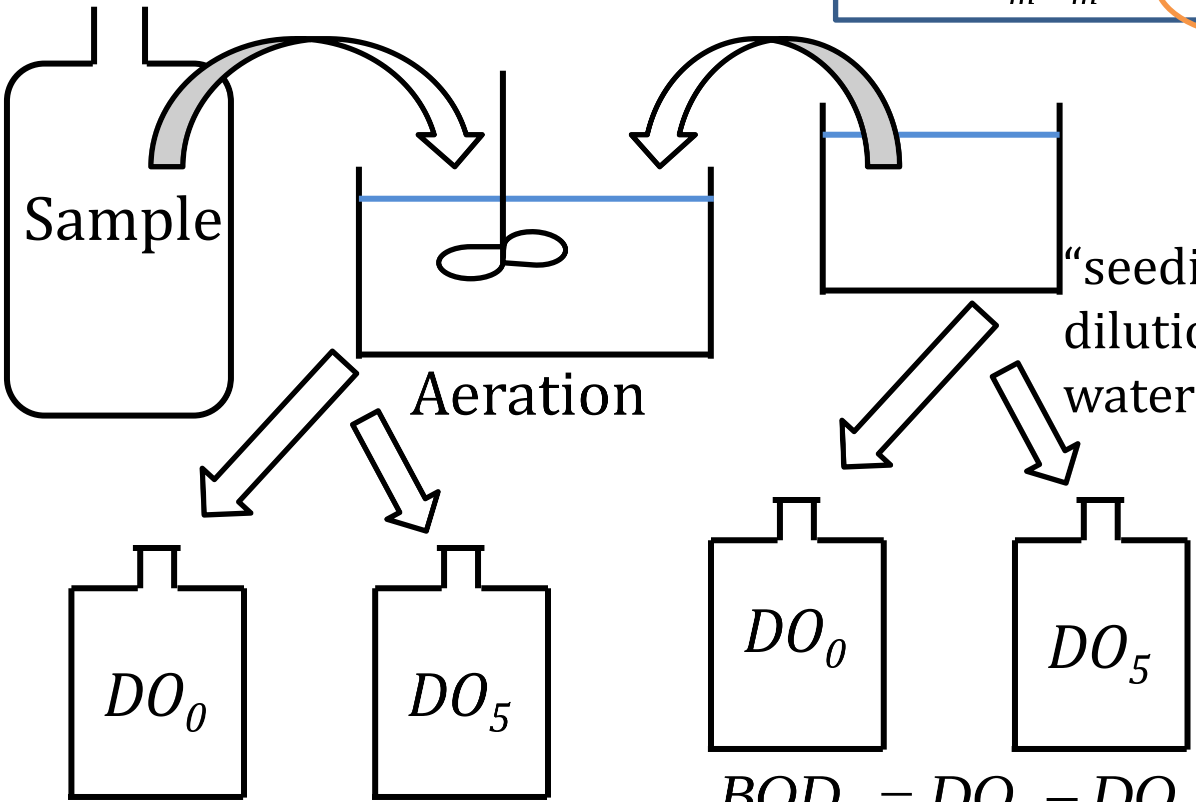
Dilution required

Laboratory measurement of BOD_5

Seeded BOD test: In some cases it is necessary to "seed" dilution water with m/o in order to ensure adequate bacterial population to carry out biodegradation

$$\boxed{BOD_m V_m = BOD_w V_w - BOD_d V_d}$$

Find BOD_w



Sample

Aeration

"seeding" dilution water

DO_0

DO_5

DO_0

DO_5

$$BOD_m = DO_0 - DO_5$$

$$BOD_d = DO_0 - DO_5$$

Example problem: BOD$_5$

<u>Problem#1</u>: A standard 5-day BOD test is run using a mix consisting of 4 parts distilled water and 1 part wastewater. The initial DO of the mix is 9.0 mg/L and the DO after 5 days is determined to be 1.0 mg/L. What is the BOD$_5$?

<u>Problem#2</u>: A mixture consisting of 30 mL of waste and 270 mL of seeded dilution water has an initial DO of 8.55 mg/L; after 5 days, it has a final DO of 2.40 mg/L. another bottle containing just the seeded dilution water has an initial DO of 8.75 mg/L and a final DO of 8.53 mg/L. What would be the 5-day BOD of the waste?

Rate of BOD exertion

The rate at which biodegradable organics are utilized by microorganisms is assumed to be a first order reaction:

$$\frac{dL_t}{dt} = -kL_t$$

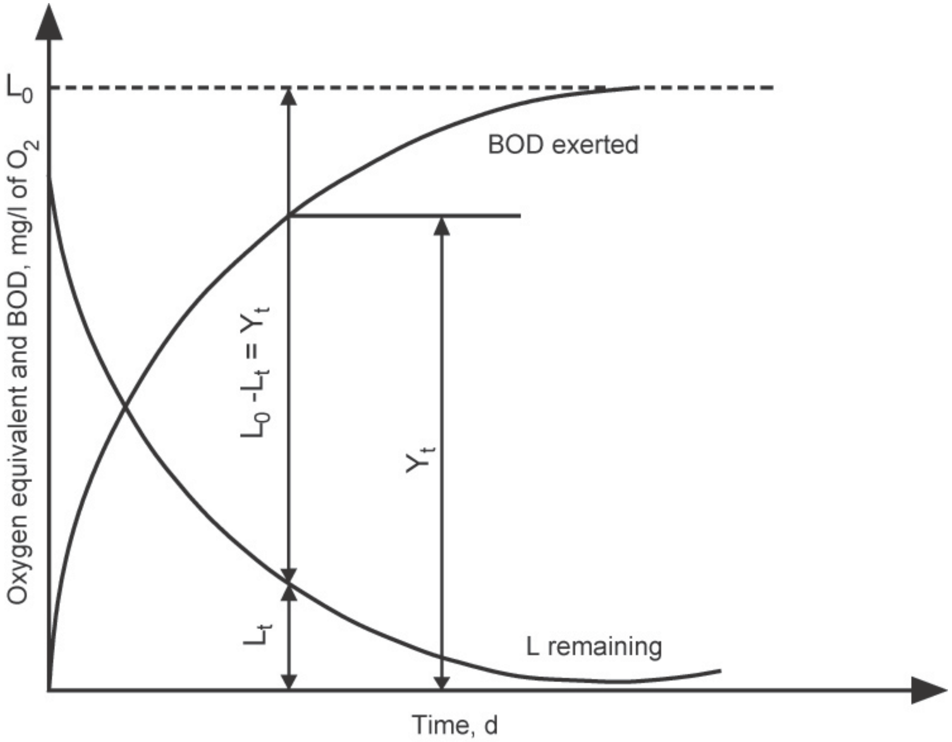
$$\Downarrow$$

$$L_t = L_0 e^{-kt}$$

L_0 = total oxygen equivalent of organics at time *t* = 0, mg/L

L_t = oxygen equivalent of organics at time *t*, mg/L

k= reaction rate constant, d^{-1}



BOD exerted after time, *t*

$$\boxed{y_t = L_0 - L_t = L_0(1 - e^{-kt})}$$

θ

Factors affecting reaction rate constant, *k*

(1) nature of the waste,
(2) ability of organisms to utilize the waste and
(3) temperature.

sample	***k* (20°C)(day^{-1})**
Raw sewage	0.35-0.70
Well-treated sewage	0.10-0.25
Polluted river water	0.10-0.25

Easily degradable organics □ k values
Complex organics □ lower k values.

$$k_T = k_{20}\theta^{T-20^\circ}$$

k_T, k_{20} are BOD rate constants at T°C and 20°C respectively
□= 1.047

Problem: Determination of BOD

The BOD_5 of a wastewater is 200 mg/L at 20°C. k at 20°C is 0.20 per day. Determine the BOD_7 of the sample at 10°C

1. *Determination of ultimate BOD* (L_0) ultimate BOD,

$$L_0 = \frac{y_5}{1-e^{-kt}} = \frac{200}{1-e^{-0.20\times 5}} = 316\,mg/L$$

2. *Determination of k at 10°C*

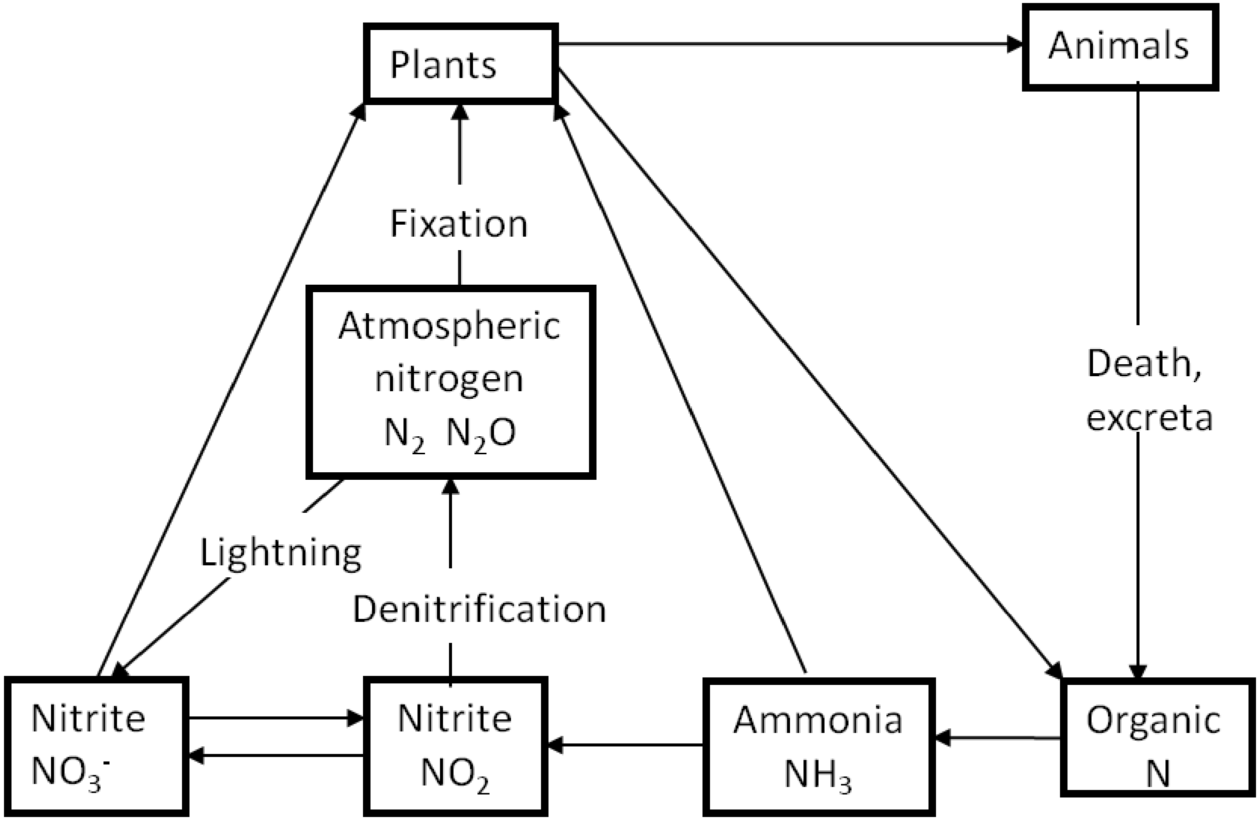
$$k_T = k_{20}\theta^{T-20^\circ} \qquad k_{10} = 0.20(1.047)^{-10} = 0.12d^{-1}$$

3. *Determination of* BOD_7 *at 10°C*

$$y_7 = L_0(1-e^{-kt}) = 316(1-e^{-0.12\times 7}) = 180.1mg/L$$

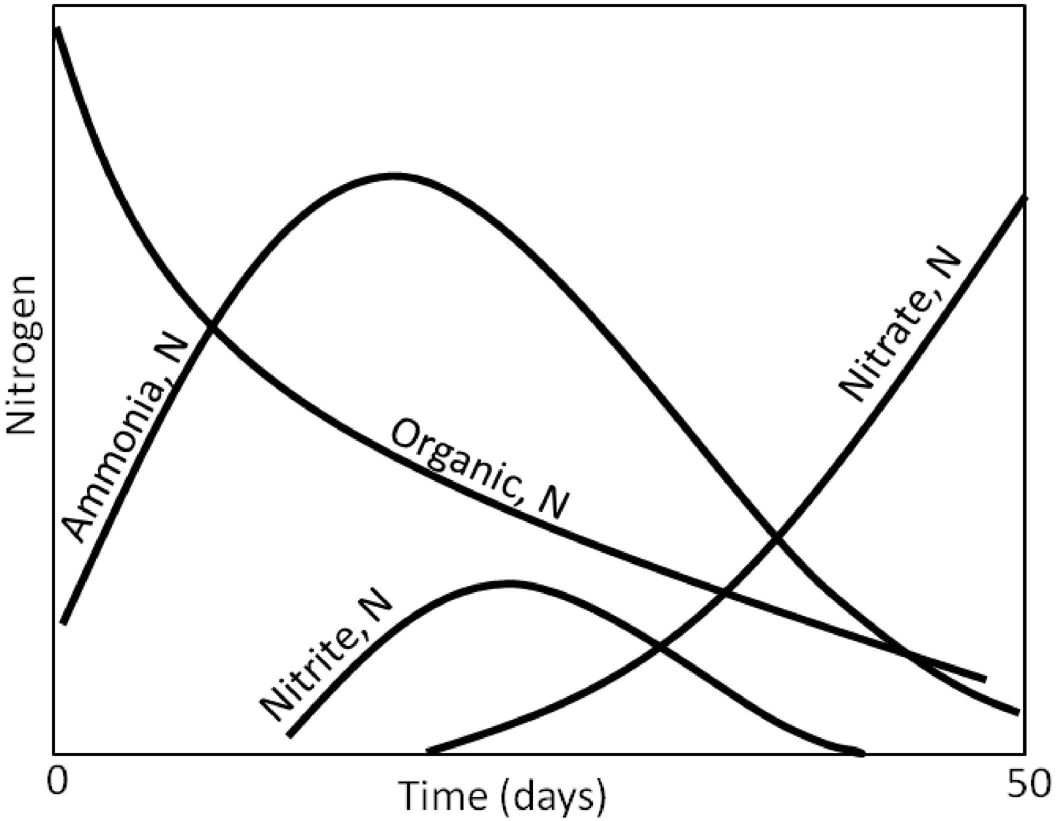
Oxygen demand due to nitrification

$$\left.\begin{aligned} 2NH_3 + 3O_2 &\xrightarrow{\textit{Nitrosomonas}} 2NO_2^- + 2H^+ + 2H_2O \\ 2NO_2^- + O_2 &\xrightarrow{\textit{Nitrobacter}} 2NO_3^- \end{aligned}\right] \text{Nitrification}$$

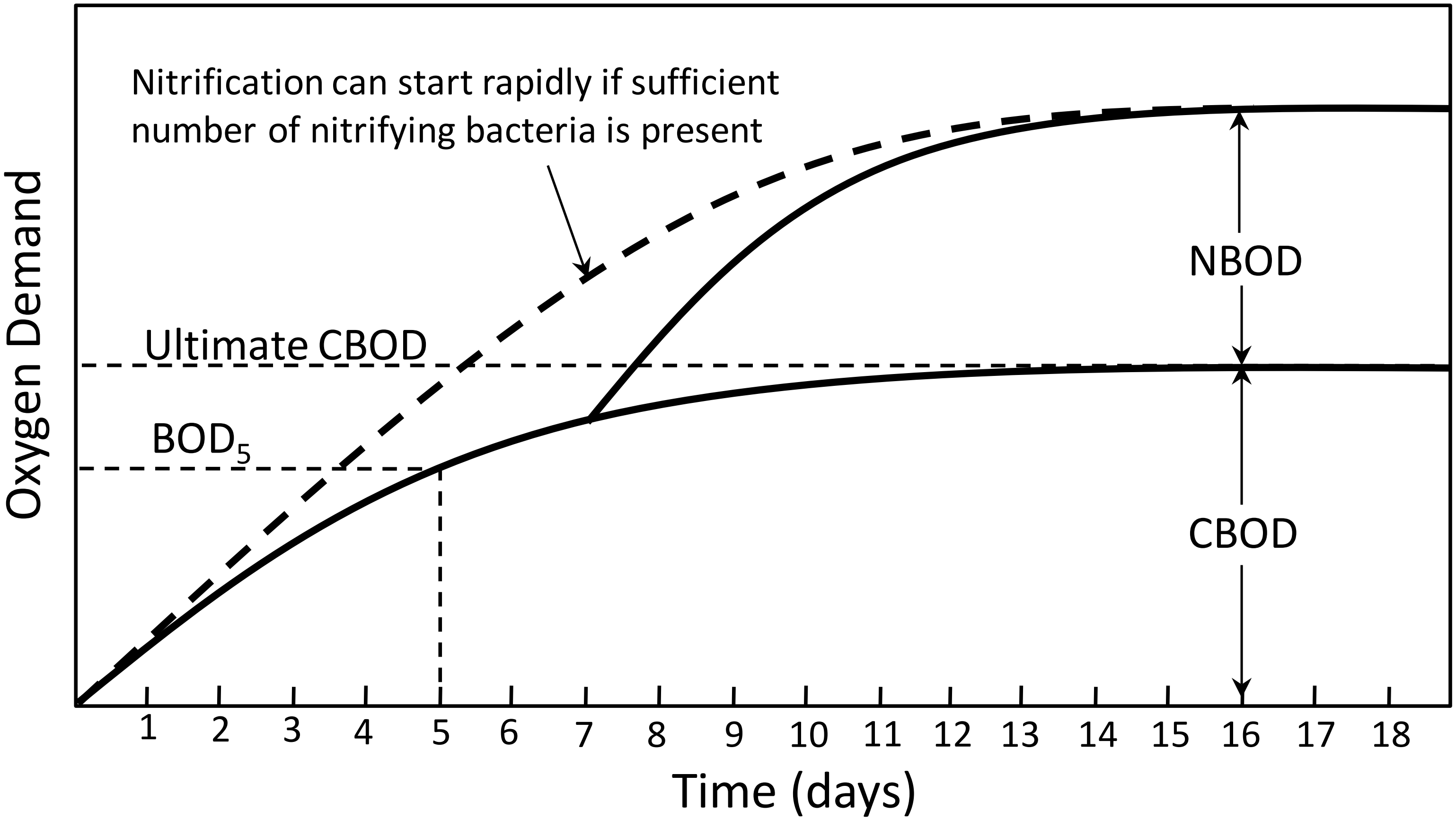


Oxygen demand due to nitrification

Nitrification occurs sequentially and it is a matter of days before the rate of oxidation of ammonia is sufficient enough to create a significant oxygen demand



CBOD and NBOD comparison



In typical municipal wastes, NBOD does not exert itself for at least 5-8 days, so **most BOD_5 tests are not affected by nitrification**

Quantifying NBOD

Some domestic wastewater has 30 mg/L of nitrogen either in the form of organic nitrogen or ammonia. Assuming that very few new cells of bacteria are formed during the nitrification of the waste, find

(i) The ultimate nitrogenous oxygen demand.

(ii) The ratio of the ultimate NBOD to the concentration of nitrogen in the waste.

$$NH_3 + 2O_2 \longrightarrow NO_3^- + H^+ + H_2O$$

$$\begin{aligned} \text{NBOD} &= 30\ \text{mgN/L} \times (17\ \text{g}\ NH_3 / 14\ \text{g N}) \times (64\text{g}\ O_2 / 17\ \text{g}\ NH_3) \\ &= 137\ \text{mg}\ O_2\text{/L} \end{aligned}$$

Total Kjeldahl Nitrogen (TKN)

The ratio of ultimate NBOD to the concentration of nitrogen in the waste

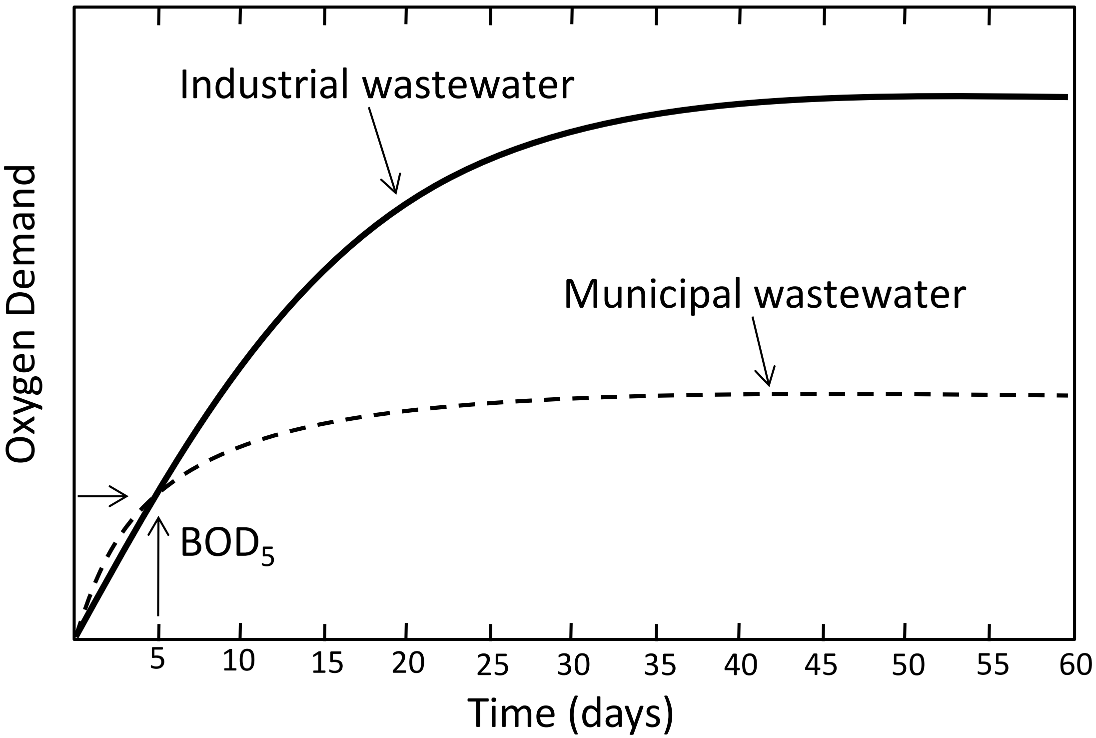
$$137\ \text{mg}\ O_2 / 30\ \text{mg N} = 4.57\ \text{mg}\ O_2\text{/mg N}$$

Ultimate NBOD ≈ 4.6 × TKN

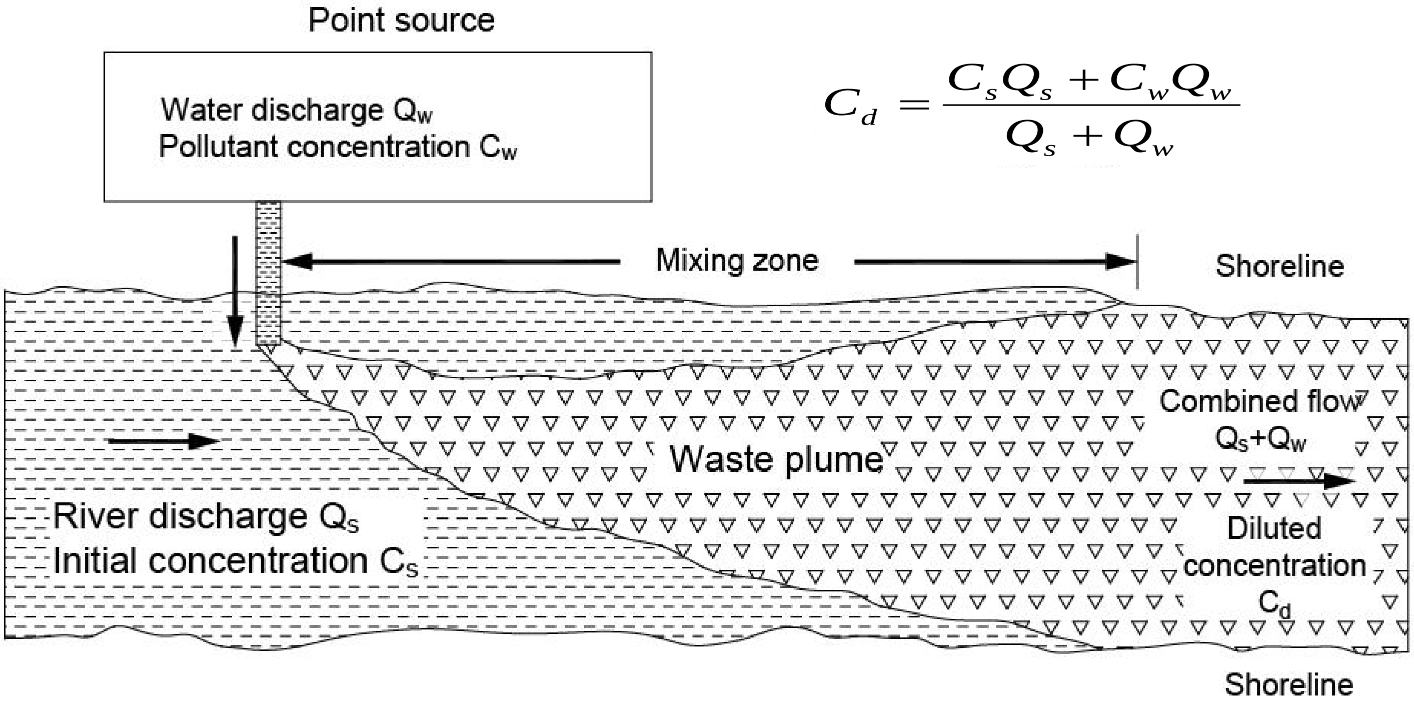
Oxygen demand: alternate measures

Chemical Oxygen Demand (COD):
Some organic materials (cellulose, phenols, benzene, and tannic acid) resist biodegradation while others (pesticides, various industrial chemicals), are nonbiodegradable

Ultimate BOD:
Different wastewaters may have the same BOD_5 but different reaction rates and hence different ultimate BOD



Mixing and Dilution



$$C_d = \frac{C_s Q_s + C_w Q_w}{Q_s + Q_w}$$

In water pollution control, it is often necessary to predict the BOD concentrations and DO levels down-stream from a sewage discharge point.

Example problem: downstream BOD

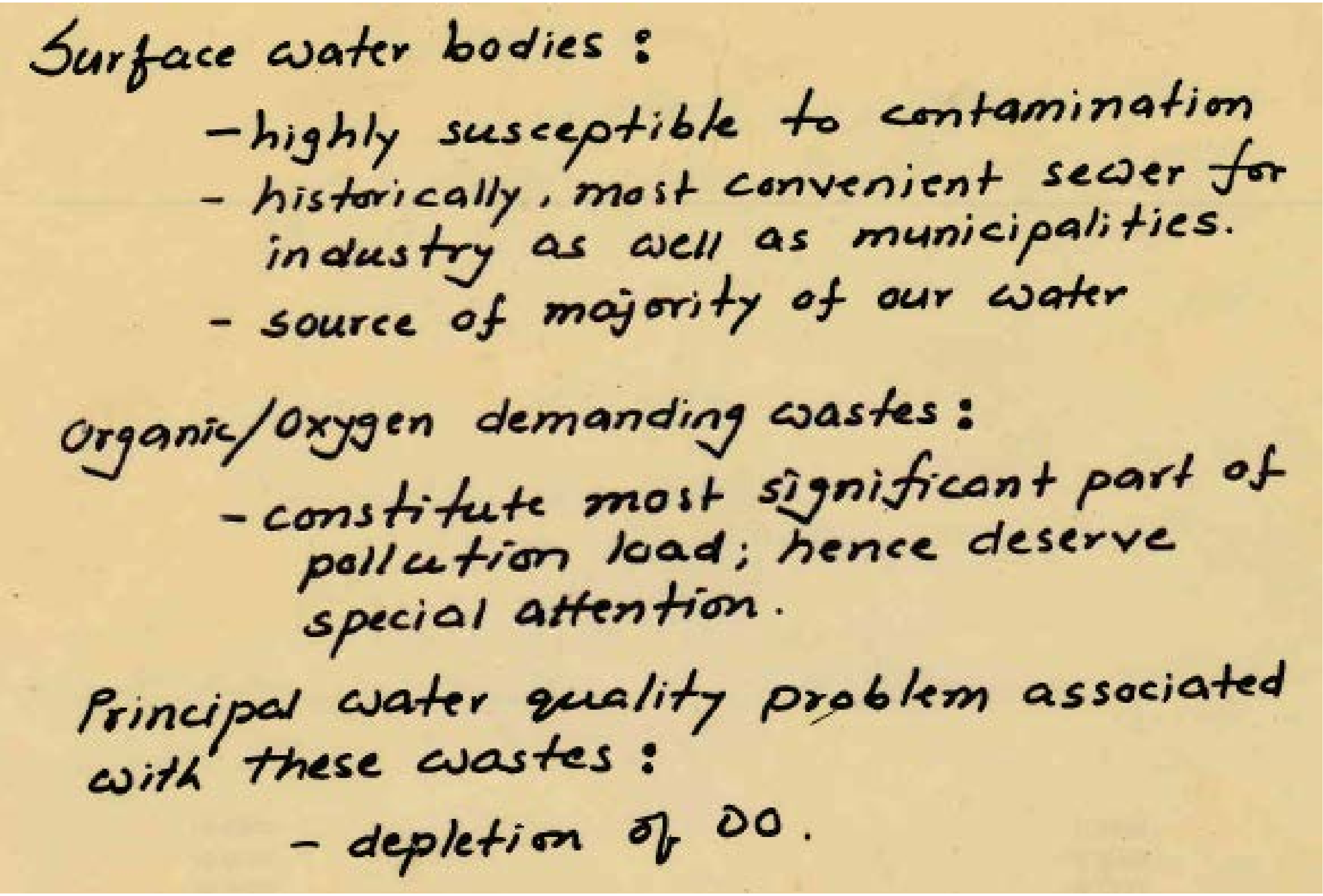
A municipal wastewater treatment plant discharges 1.20 m^3/s of treated effluent having an ultimate BOD of 60.0 mg/L into a stream that has a flow of 9.3 m^3/s and a BOD of its own equal to 6.0 mg/L. The deoxygenation constant k_d is 0.20/day.

(a) Assuming complete and instantaneous mixing, estimate the ultimate BOD of the river just downstream from the outfall.

(b) If the stream has constant cross section so that it flows at a fixed speed equal to 0.30 m/s, estimate the BOD of the stream at a distance 40,000 m downstream.

Answer: (a) 12.2 mg/L
(b) 8.96 mg/L

Surface Water (Rivers and Streams) Pollution and DO Availability



Surface water bodies:

- highly susceptible to contamination
- historically, most convenient sewer for industry as well as municipalities.
- source of majority of our water

Organic/Oxygen demanding wastes:

- constitute most significant part of pollution load; hence deserve special attention.

Principal water quality problem associated with these wastes:

- depletion of DO.

Modeling Effect of O_2 Demanding Waste on Rivers:
Important sources and sinks of DO in rivers

Sources:

1. Reaeration from atmosphere
2. Photosynthetic O_2 production by aquatic plants
3. DO in incoming tributaries

Sinks:

1. Oxidation of organic wastes (both carbonaceous and nitrogenous)
2. Use of O_2 for respiration of aquatic plants
3. Oxygen demand of sediment

Two key processes are involved in the O_2 mass balance in rivers:

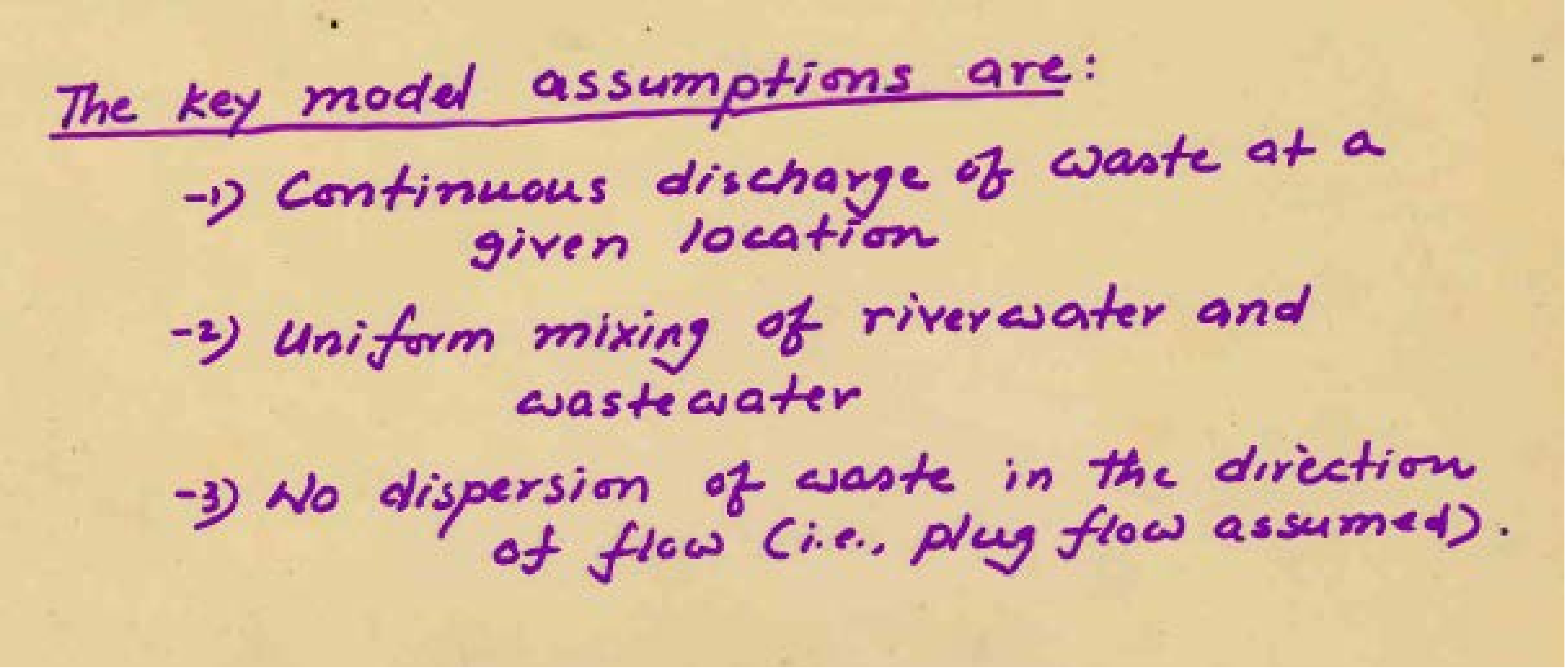
Deoxygenation:

i.e., the removal of oxygen by microorganisms during biodegradation of organic wastes

Reoxygenation:

i.e., the replenishment of oxygen through reaeration at the surface of the river

Modeling Effect of O_2 Demanding Waste on Rivers/Streams:



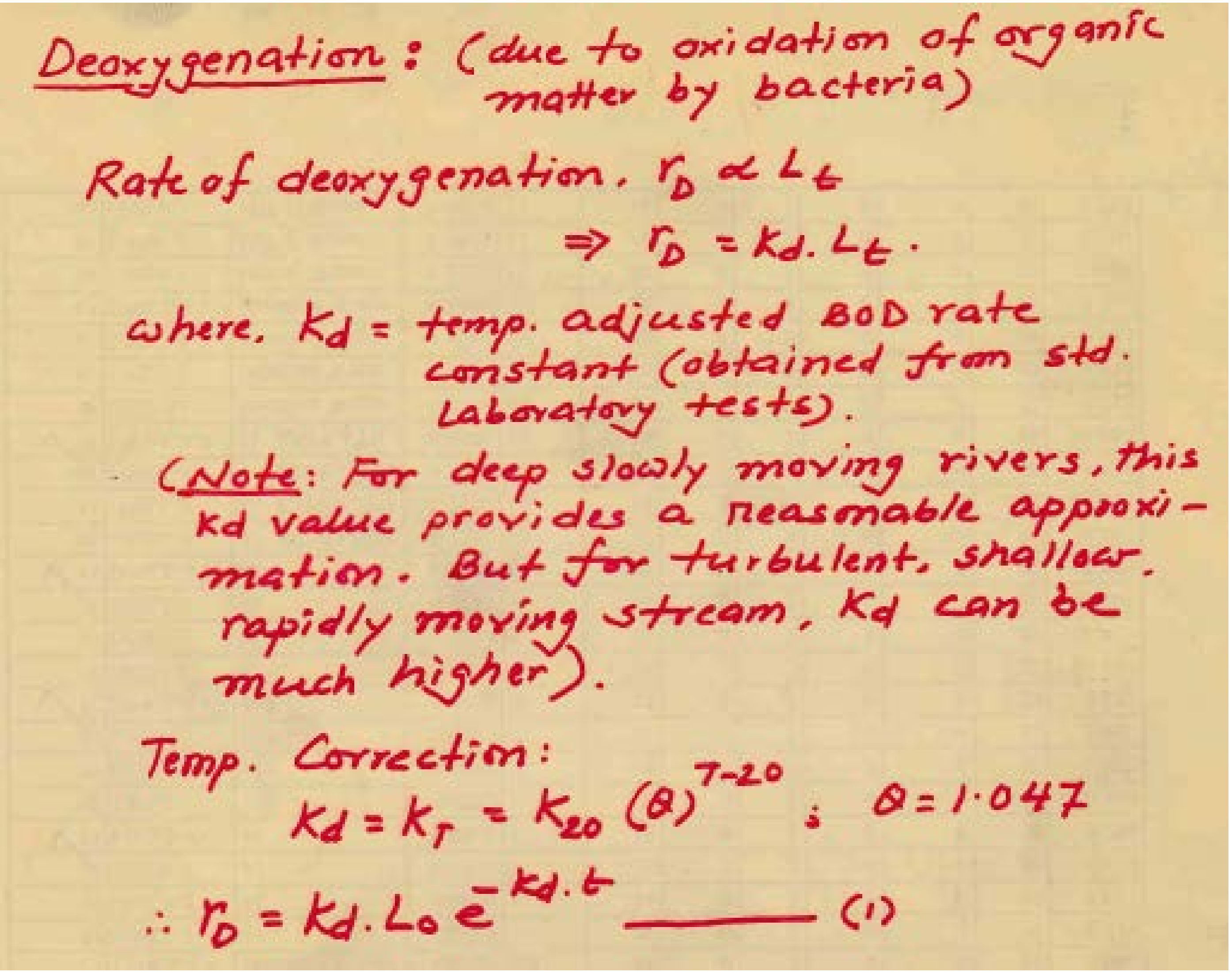
The key model assumptions are:

-1) Continuous discharge of waste at a given location

-2) Uniform mixing of riverwater and wastewater

-3) No dispersion of waste in the direction of flow (i.e., plug flow assumed).

Model Equations



Deoxygenation: (due to oxidation of organic matter by bacteria)

Rate of deoxygenation, $r_D \propto L_t$

$$\Rightarrow r_D = k_d . L_t .$$

where, k_d = temp. adjusted BOD rate constant (obtained from std. laboratory tests).

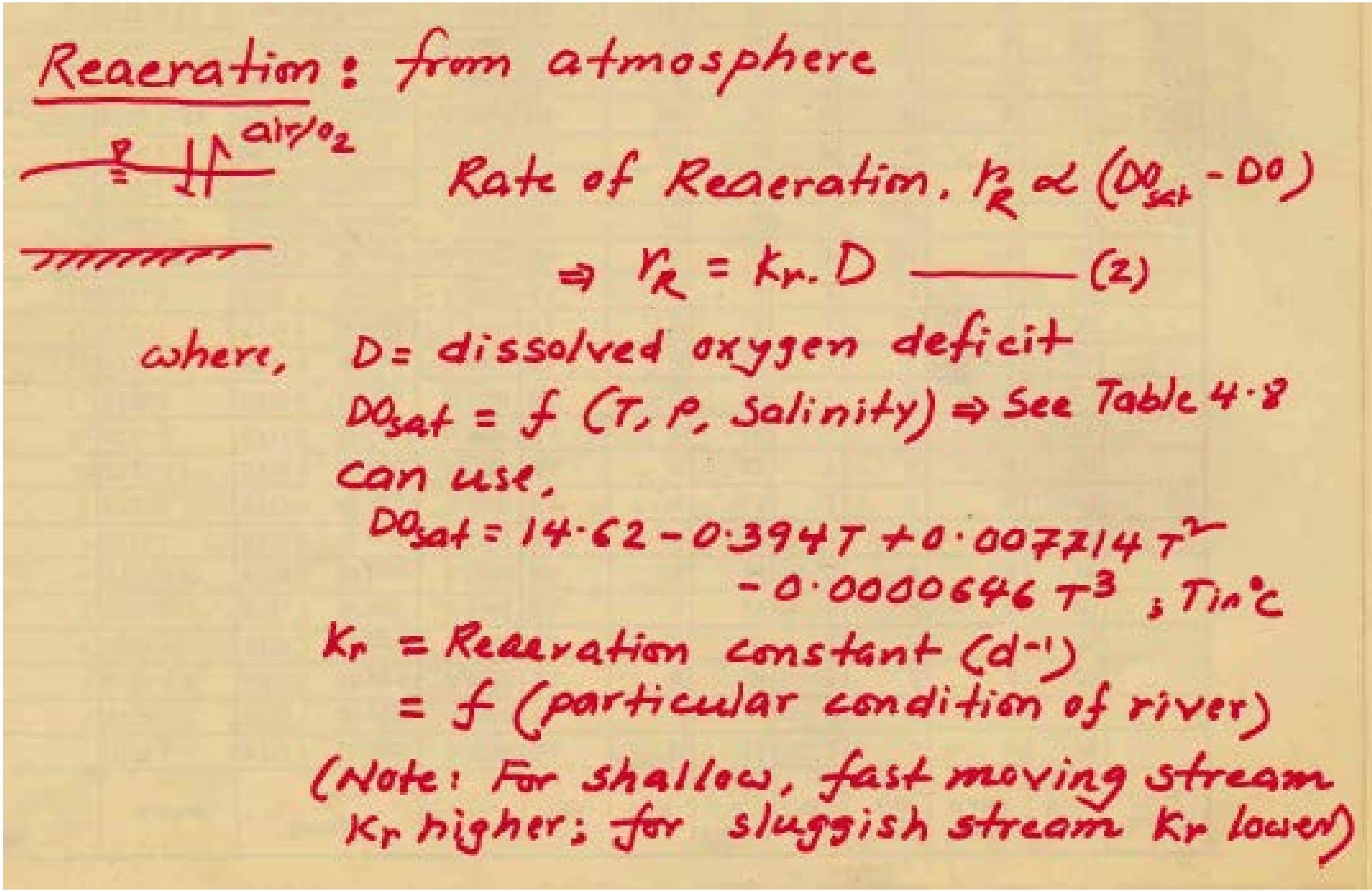
(**Note**: For deep slowly moving rivers, this k_d value provides a reasonable approximation. But for turbulent, shallow, rapidly moving stream, k_d can be much higher).

Temp. Correction:

$$k_d = k_T = k_{20} (\theta)^{T-20} \; ; \; \theta = 1.047$$

$$\therefore r_D = k_d . L_0 e^{-k_d . t} \quad \text{———} \quad (1)$$

Model Equations ……..



Reaeration: from atmosphere

Rate of Reaeration, $r_R \propto (DO_{sat} - DO)$

$\Rightarrow r_R = k_r \cdot D$ ——— (2)

where, D= dissolved oxygen deficit

$DO_{sat} = f\,(T, P, \text{Salinity}) \Rightarrow$ See Table 4·8

can use,

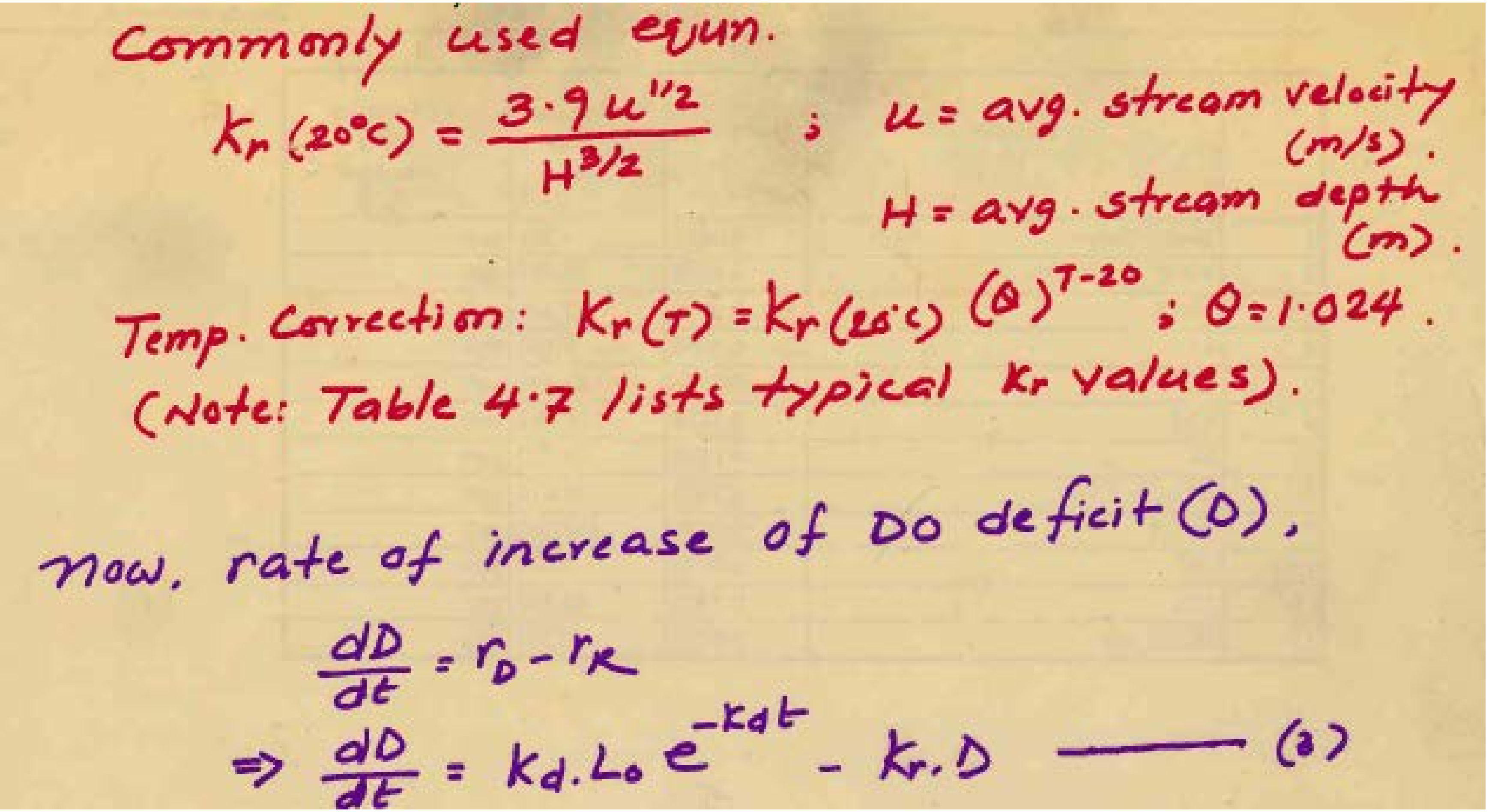
$$DO_{sat} = 14{\cdot}62 - 0{\cdot}394\,T + 0{\cdot}007714\,T^2 - 0{\cdot}0000646\,T^3$$; T in °C

K_r = Reaeration constant (d^{-1})

= f (particular condition of river)

(Note: For shallow, fast moving stream K_r higher; for sluggish stream K_r lower)

Model Equations ……..



Commonly used equn.

$$k_r(20°C) = \frac{3.9\,u^{1/2}}{H^{3/2}}$$; u = avg. stream velocity (m/s).

H = avg. stream depth (m).

Temp. Correction: $K_r(T) = K_r(20°C)\,(\theta)^{T-20}$; $\theta = 1.024$.

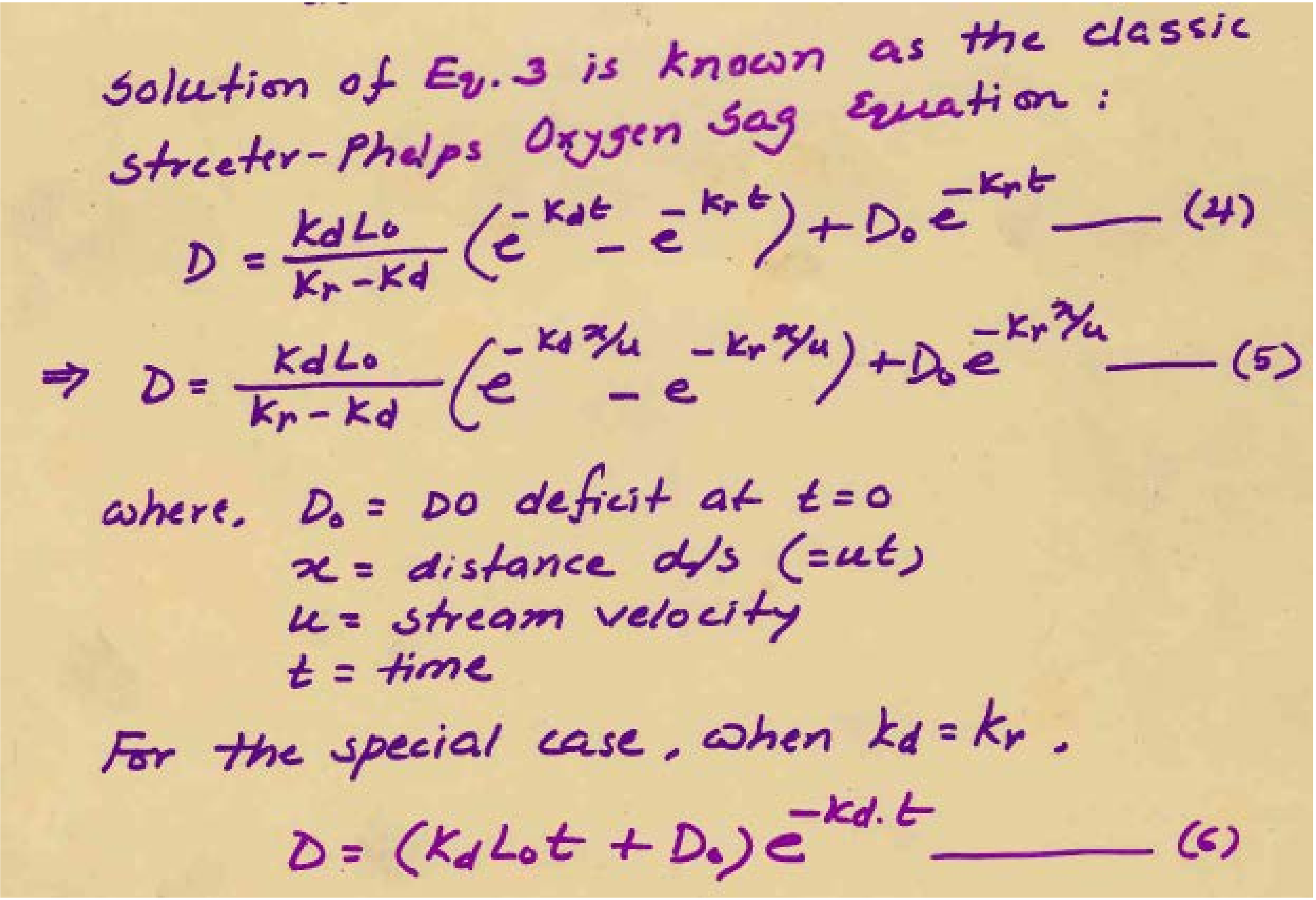
(Note: Table 4.7 lists typical k_r values).

now, rate of increase of DO deficit (D),

$$\frac{dD}{dt} = r_D - r_R$$

$$\Rightarrow \frac{dD}{dt} = k_d.L_0\,e^{-k_d t} - k_r.D \quad \text{———} \quad (2)$$

Model Equations ……..



solution of Eq. 3 is known as the classic Streeter-Phelps Oxygen sag Equation :

$$D = \frac{k_d L_o}{k_r - k_d}\left(e^{-k_d t} - e^{-k_r t}\right) + D_o e^{-k_r t} \quad \text{———} \quad (4)$$

$$\Rightarrow D = \frac{k_d L_o}{k_r - k_d}\left(e^{-k_d x/u} - e^{-k_r x/u}\right) + D_o e^{-k_r x/u} \quad \text{———} \quad (5)$$

where, D_o = DO deficit at $t=0$

x = distance d/s ($=ut$)

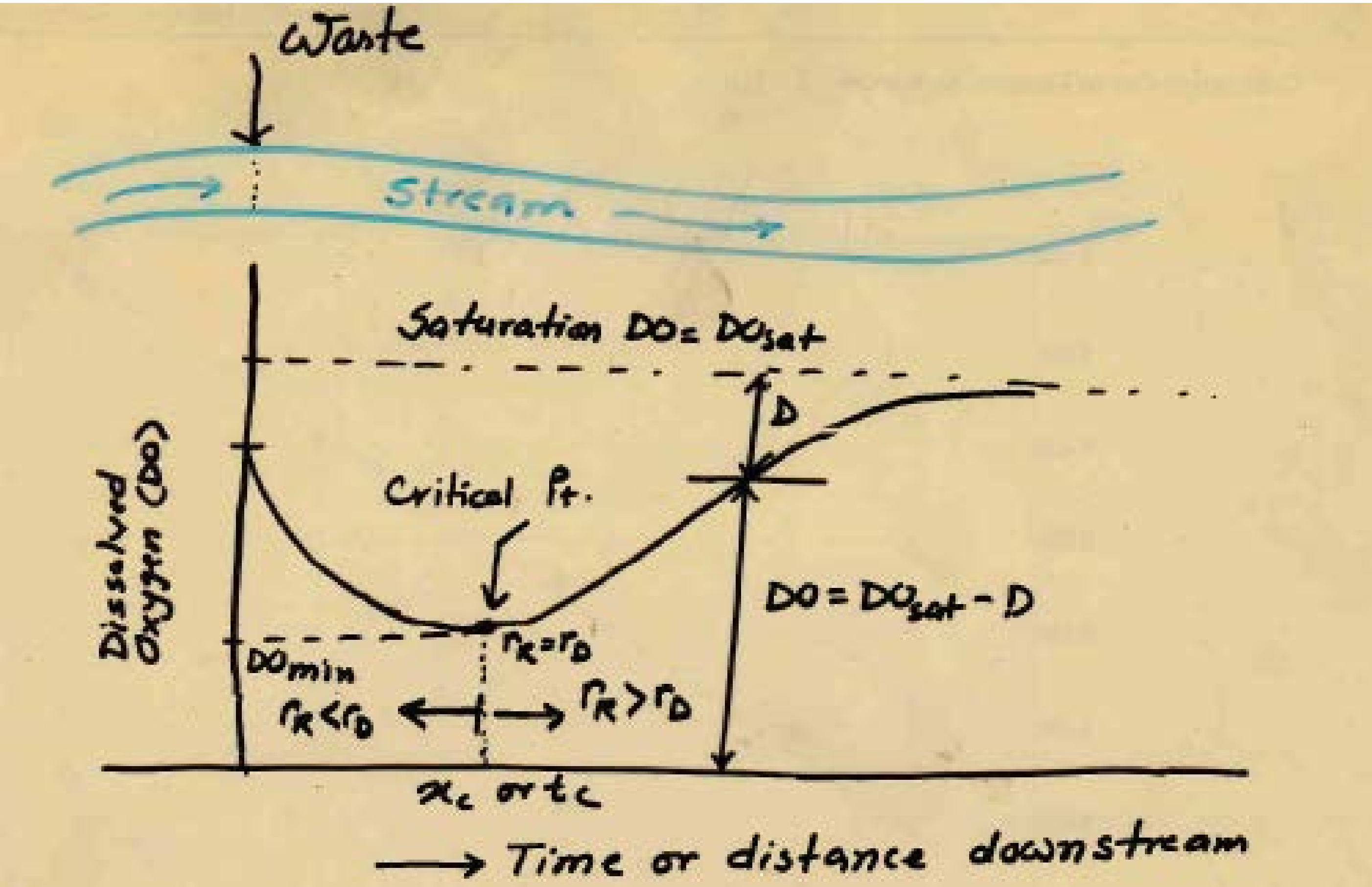
u = stream velocity

t = time

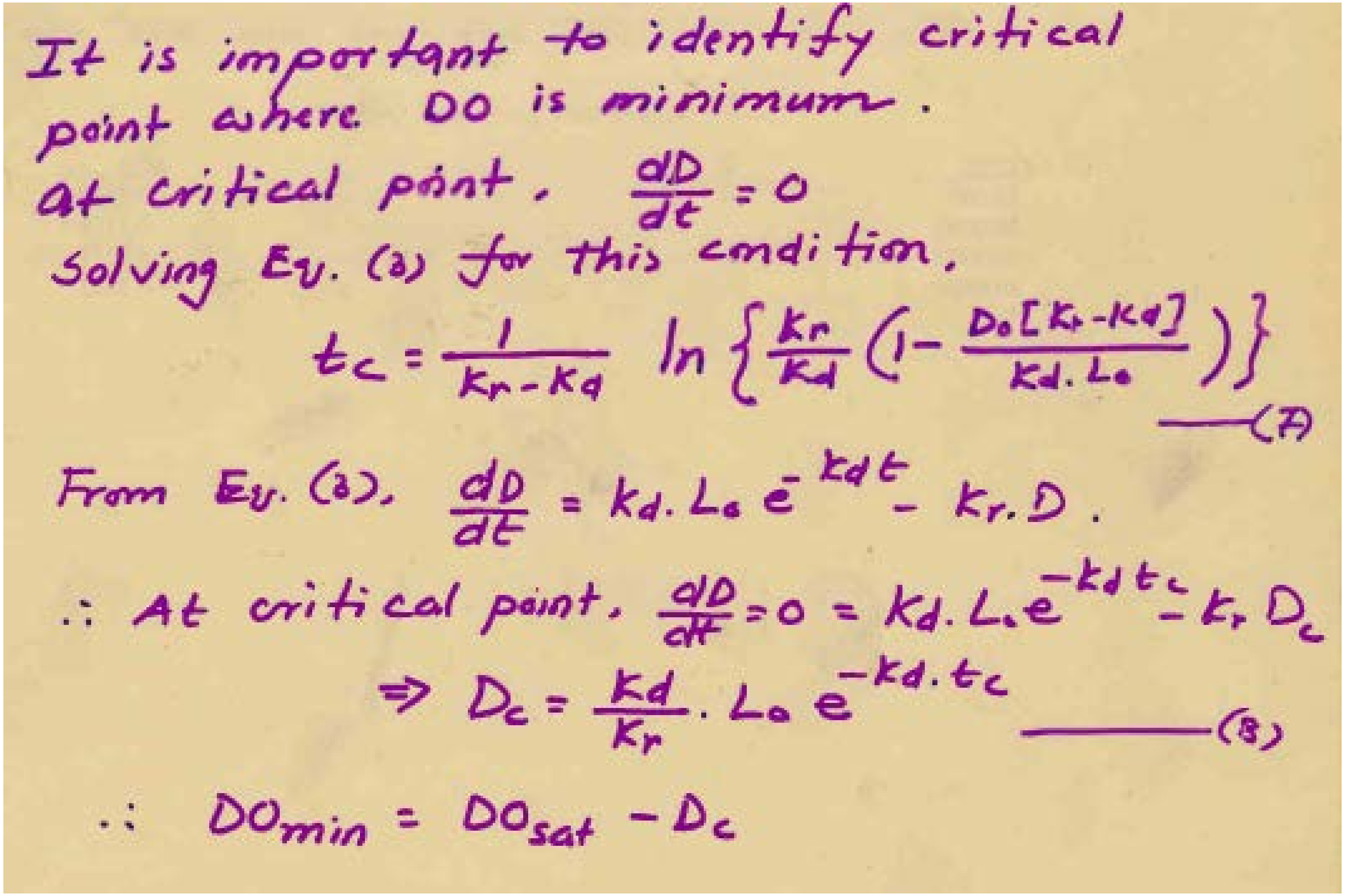
For the special case, when $k_d = k_r$,

$$D = (k_d L_o t + D_o)e^{-k_d . t} \quad \text{————} \quad (6)$$

DO Sag Curve


Waste
Stream
Saturation DO = DO_{sat}
D
Critical Pt.
DO = DO_{sat} - D
Dissolved Oxygen (DO)
DO_{min}
$r_R = r_D$
$r_R < r_D$
$r_R > r_D$
x_c or t_c
Time or distance downstream

Critical Point and Minimum DO



It is important to identify critical point where DO is minimum.

at critical point, $\frac{dD}{dt} = 0$

Solving Eq. (2) for this condition,

$$t_c = \frac{1}{k_r - k_d} \ln \left\{ \frac{k_r}{k_d} \left(1 - \frac{D_0 [k_r - k_d]}{k_d . L_0} \right) \right\} \qquad \text{—— (A)}$$

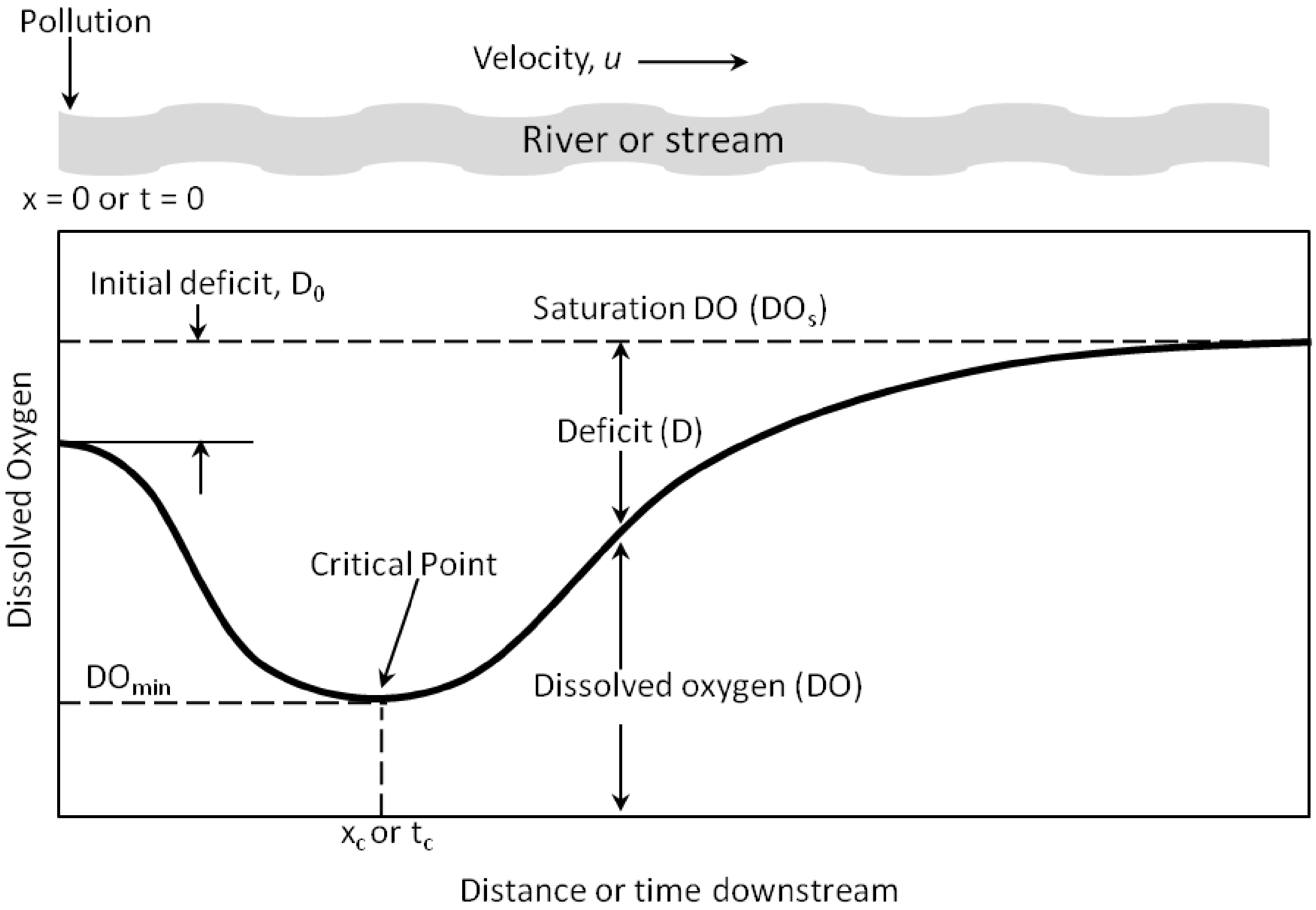
From Eq. (2), $\frac{dD}{dt} = k_d . L_0 e^{-k_d t} - k_r . D$.

$\therefore$ At critical point, $\frac{dD}{dt} = 0 = k_d . L_0 e^{-k_d t_c} - k_r D_c$

$$\Rightarrow D_c = \frac{k_d}{k_r} . L_0 e^{-k_d . t_c} \qquad \text{—— (B)}$$

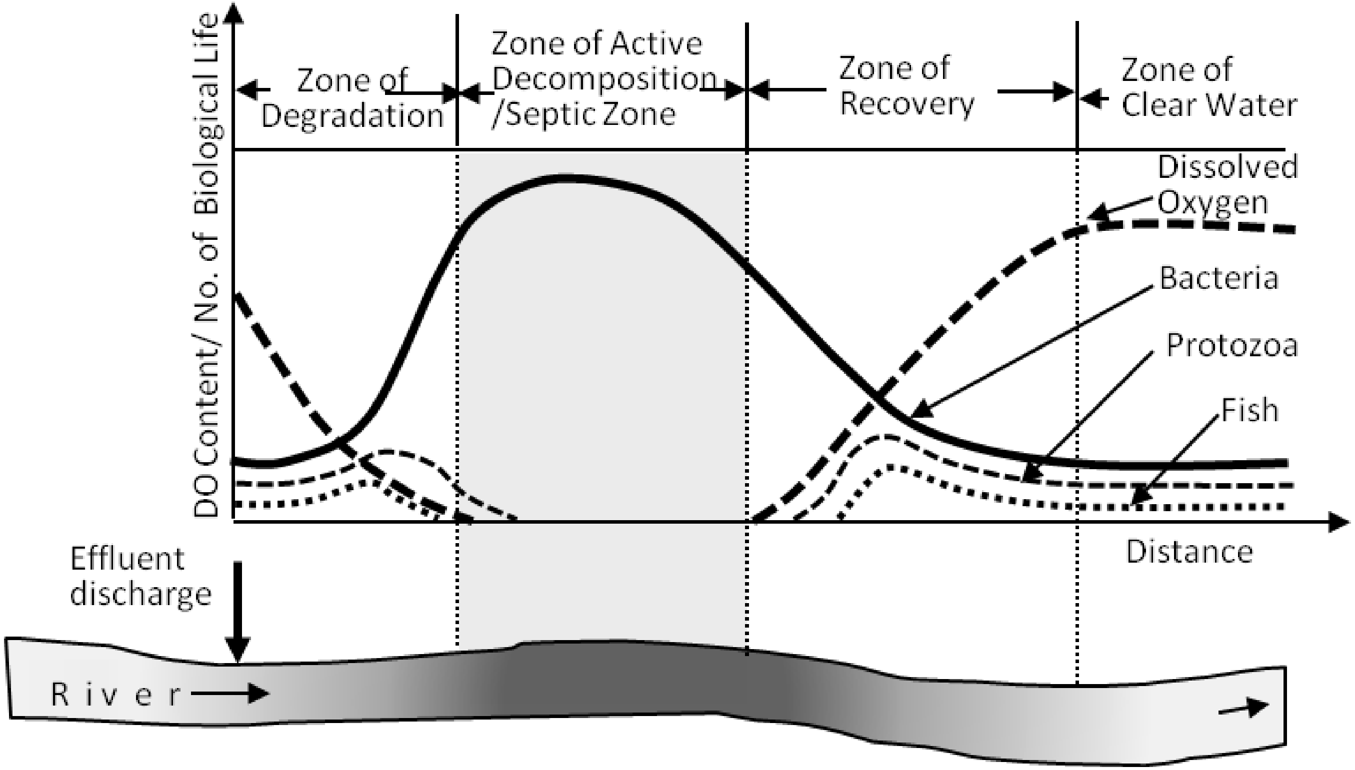
$\therefore$ $DO_{min} = DO_{sat} - D_c$

Streeter-Phelps oxygen sag curve



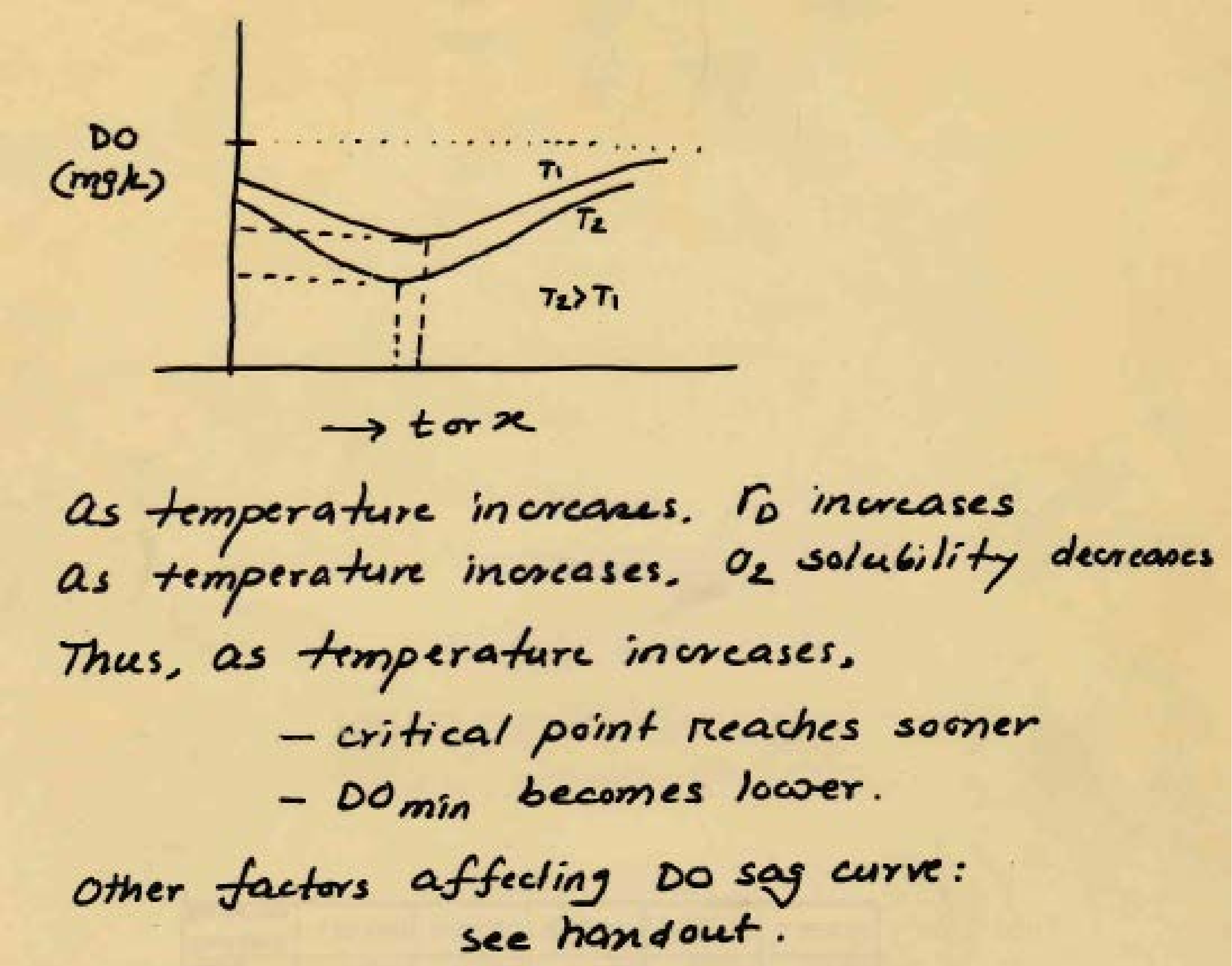
Time to critical point $$t_c = \frac{1}{k_r - k_d} \ln\left\{ \frac{k_r}{k_d} \left[1 - \frac{D_0 (k_r - k_d)}{k_d L_0} \right] \right\}$$

Zones of Pollution



Pollution and self-purification of stream and changes in the aquatic ecology by the disposal of sewage/industrial wastewater

Effect of Temperature on DO Sag Curve



as temperature increases, r_D increases

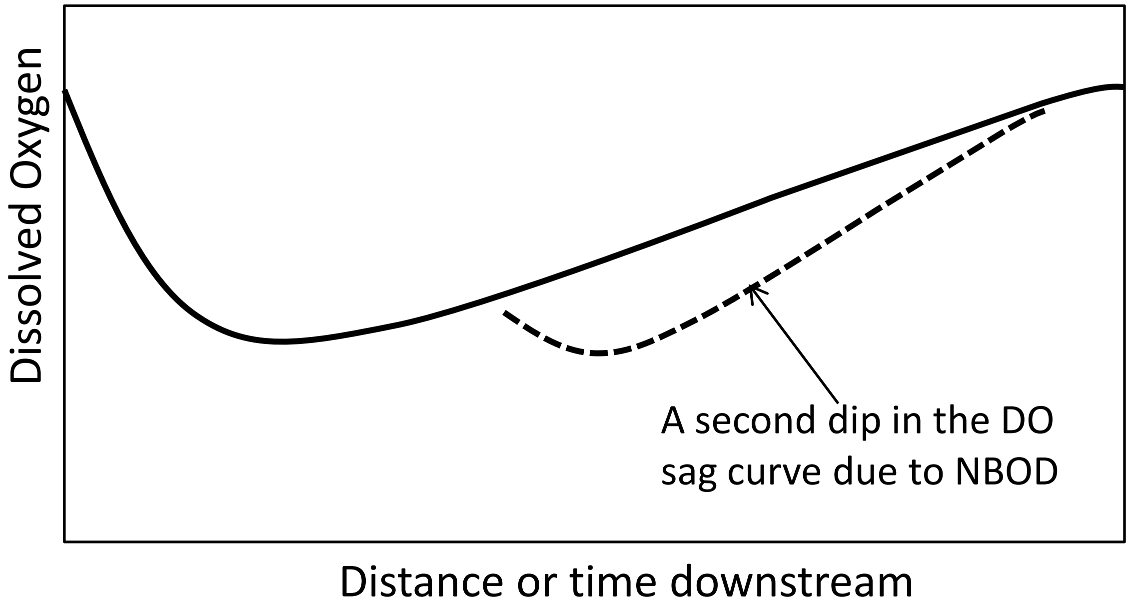
as temperature increases, O_2 solubility decreases

Thus, as temperature increases,

- critical point reaches sooner
- DO_{min} becomes lower.

Other factors affecting DO sag curve:
see handout.

Effect of NBOD on DO Sag Curve



An additional term in the DO sag equation

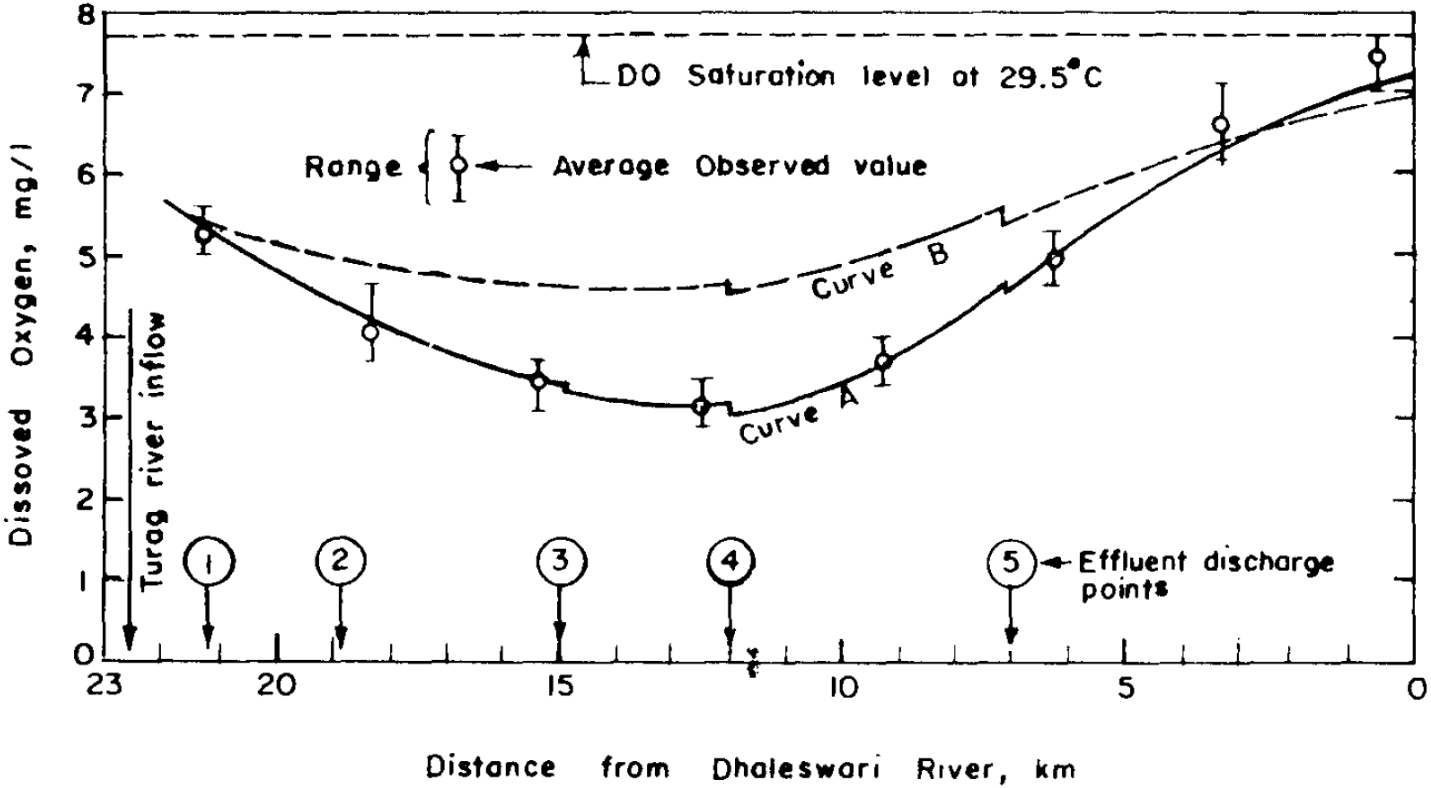
$$D = \frac{k_d L_0}{k_r - k_d}\left(e^{-k_d t} - e^{-k_r t}\right) + D_0 e^{-k_r t} + \boxed{\frac{k_n L_n}{k_r - k_n}\left(e^{-k_n t} - e^{-k_r t}\right)}$$

Minimum DO cannot be determined analytically (trial and error solution required)

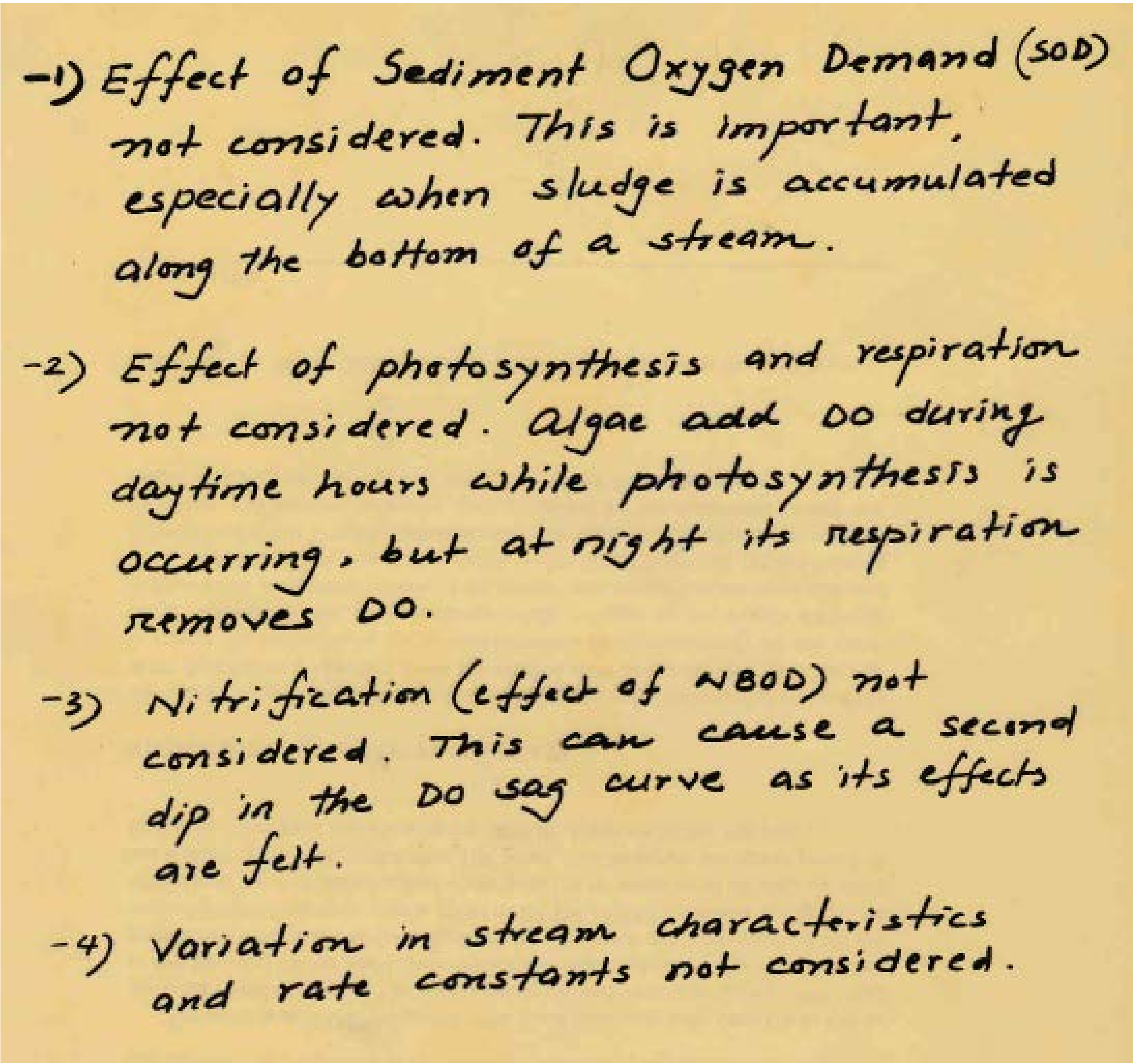
k_n = the nitrogenous deoxygenation rate (day^{-1})
L_n = ultimate initial NBOD (mg/L)

Multiple point sources

- Divide the river into multiple reaches with each point source located at the beginning of the reach
- The parameters (DO, BOD etc.) computed at the end of each reach serve as initial conditions for the subsequent reach



Limitations of Oxygen Sag Equations



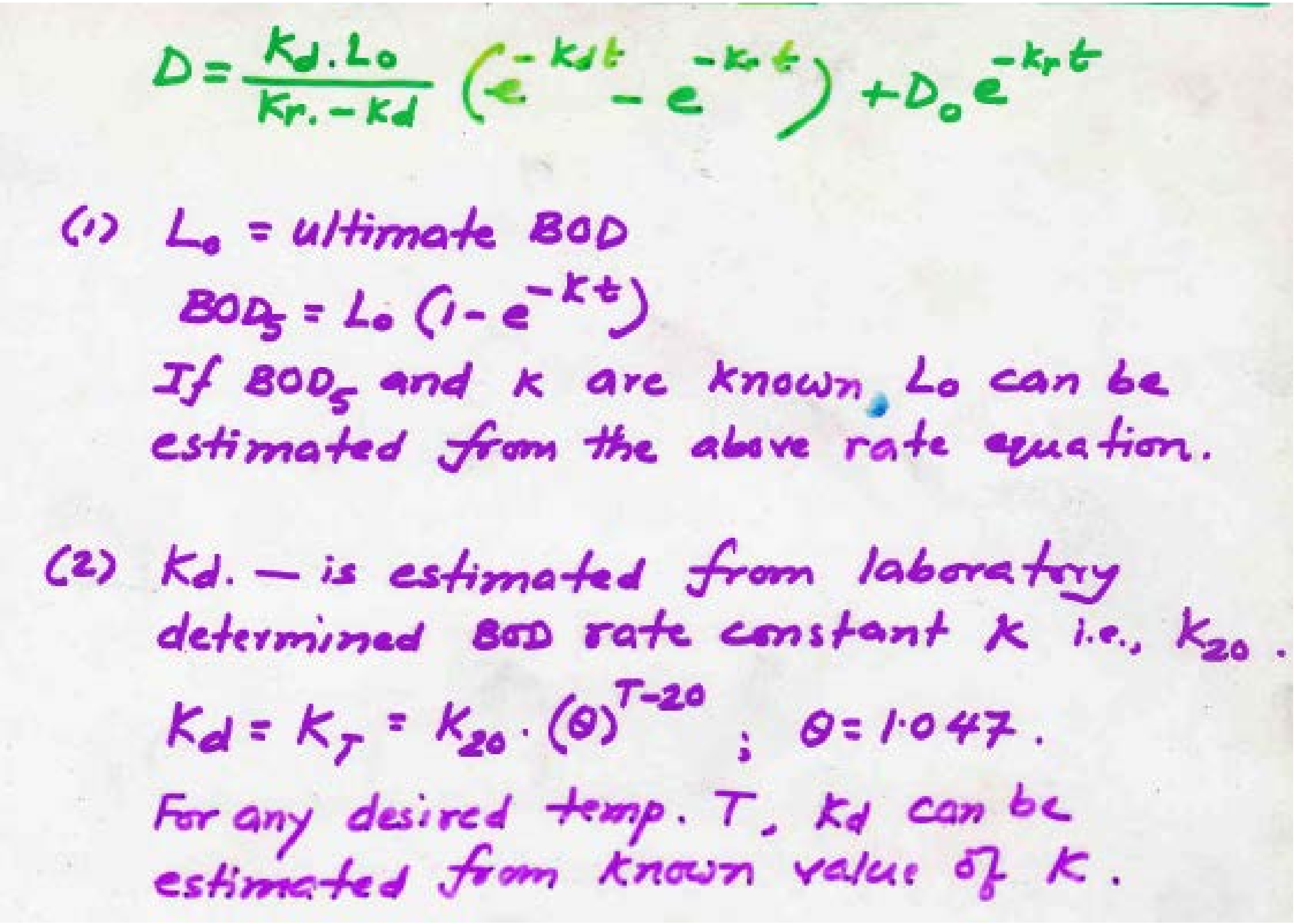
-1) Effect of Sediment Oxygen Demand (SOD) not considered. This is important, especially when sludge is accumulated along the bottom of a stream.

-2) Effect of photosynthesis and respiration not considered. Algae add DO during daytime hours while photosynthesis is occurring, but at night its respiration removes DO.

-3) Nitrification (effect of NBOD) not considered. This can cause a second dip in the DO sag curve as its effects are felt.

-4) Variation in stream characteristics and rate constants not considered.

Estimation of Parameters of DO Sag Equations



$$D = \frac{K_d . L_0}{K_r . - K_d}\left(e^{-K_d t} - e^{-K_r t}\right) + D_0 e^{-K_r t}$$

(1) L_0 = ultimate BOD

$BOD_5 = L_0 (1 - e^{-kt})$

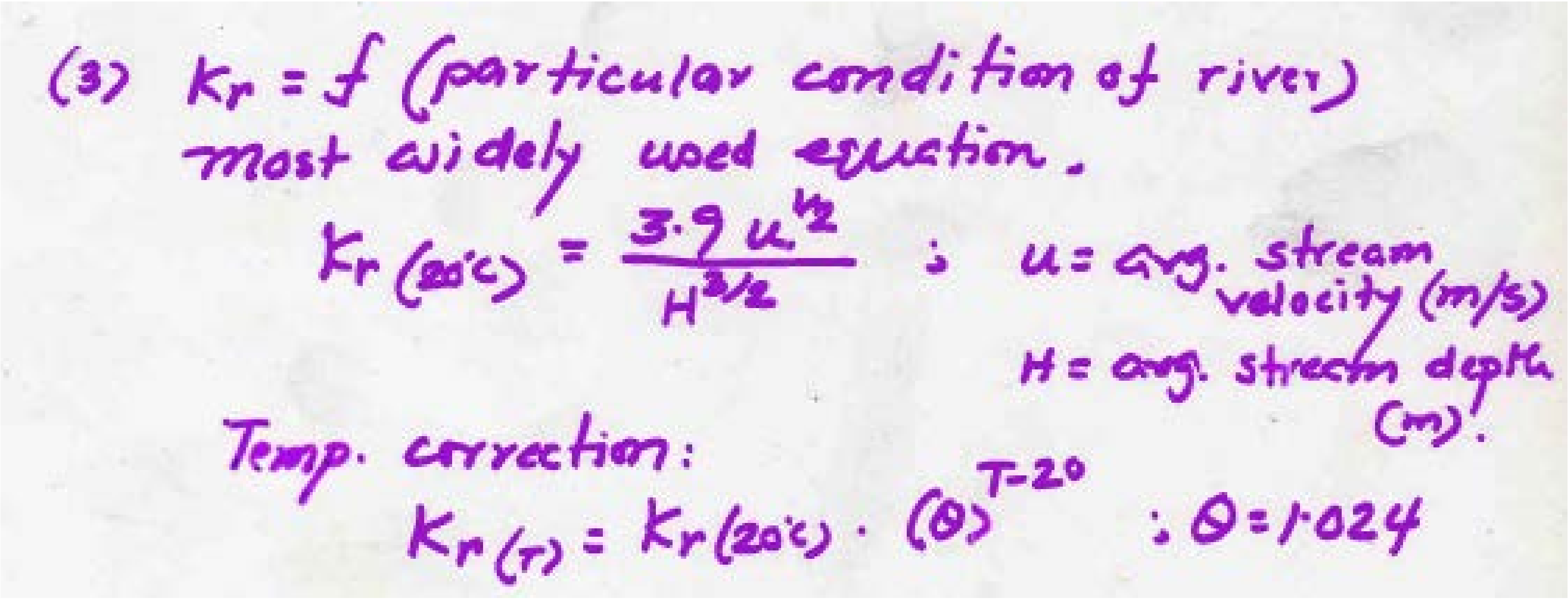
If BOD_5 and k are known, L_0 can be estimated from the above rate equation.

(2) K_d. — is estimated from laboratory determined BOD rate constant k i.e., k_{20}.

$K_d = K_T = K_{20} \cdot (\theta)^{T-20}$; $\theta = 1{\cdot}047$.

For any desired temp. T, K_d can be estimated from known value of k.

Estimation of Parameters of DO Sag Equations …….



(3) $k_r = f$ (particular condition of river)
most widely used equation.

$$k_{r(20^\circ C)} = \frac{3.9\, u^{1/2}}{H^{3/2}}$$

; u = avg. stream velocity (m/s)
H = avg. stream depth (m).

Temp. correction:

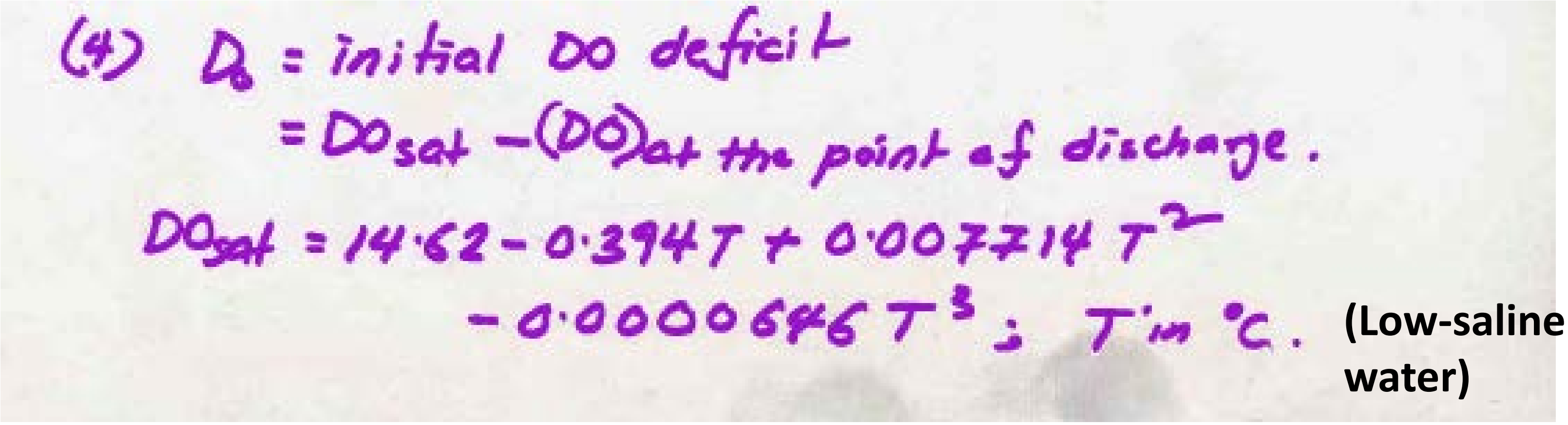
$$k_{r(T)} = k_{r(20^\circ C)} \cdot (\theta)^{T-20}$$

; $\theta = 1.024$

Typical k_r values for different water bodies

Water body	**Range of k_r at 20°C (base e) (day^{-1})**
Small ponds and backwaters	0.10-0.23
sluggish streams and large lakes	0.23-0.35
Large streams of low velocity	0.35-0.46
Large streams of normal velocity	0.46-0.69
Swift streams	0.69-1.15
Rapids and waterfalls	>1.15

Estimation of Parameters of DO Sag Equations …….



(4) D_0 = initial DO deficit

$= DO_{sat} - (DO)_{at\ the\ point\ of\ discharge}$.

$DO_{sat} = 14{\cdot}62 - 0{\cdot}3947T + 0{\cdot}007714T^2$

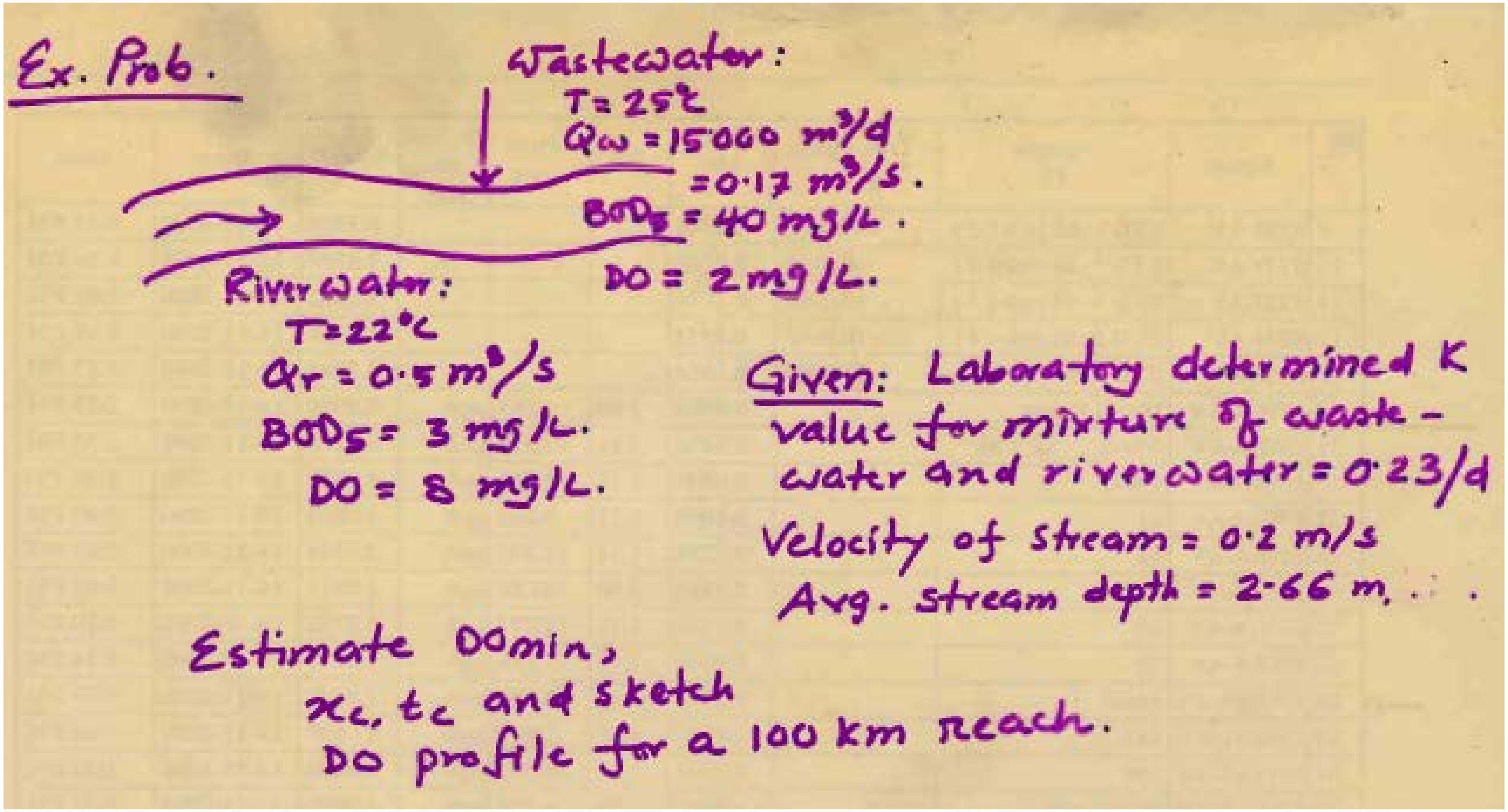
$- 0{\cdot}0000646T^3$; T in °C.

(Low-saline water)

Solubility of oxygen in water at 1 atm

Temperture (°C)	Chloride concentration in water (mg/L)			
	0	5000	10000	15000
0	14.62	13.73	12.89	12.10
5	12.77	12.02	11.32	10.66
10	11.29	10.66	10.06	9.49
15	10.08	9.54	9.03	8.54
20	9.09	8.62	8.17	7.75
25	8.26	7.85	7.46	7.08
30	7.56	7.19	6.85	6.51

Example Problem:



Ex. Prob.

Wastewater:
$T = 25°C$
$Q_w = 15000 \ m^3/d$
$= 0.17 \ m^3/s.$
$BOD_5 = 40 \ mg/L.$
$DO = 2 \ mg/L.$

Riverwater:
$T = 22°C$
$Q_r = 0.5 \ m^3/s$
$BOD_5 = 3 \ mg/L.$
$DO = 8 \ mg/L.$

Given: Laboratory determined K value for mixture of waste-water and riverwater $= 0.23/d$

Velocity of stream $= 0.2$ m/s

Avg. stream depth $= 2.66$ m.

Estimate DO_{min}, x_c, t_c and sketch DO profile for a 100 km reach.

Pollution Control: Factors affecting self-purification

❑For O_2 demanding wastes: dilution, time of passage, water temp., waste characteristics, stream characteristics

❑For pathogens: dilution, time of exposure, water temp

❑For POPs: dilution, association with stream sediment

❑Physical channel characteristics: shallow and steep channels have better aeration compared to deep meandering rivers

Organic wastes comprise the most significant part of pollution load. **If waste assimilation capacity of a stream is adequate to handle organic wastes, it is usually adequate to handle other classifications of waste as well.**

Pollution control measures

- ☐ Reduce concentration of pollutants by (1) wastewater treatment (2) industrial in-plant process control
- ☐ Controlling u/s point and non-point sources
- ☐ Reduce effluent volume by process modification
- ☐ Increase u/s flow by flow augmentation (releasing water from u/s storage reservoirs or from flow diversion)
- ☐ Increasing environmental/in-stream degradation rate of substances (e.g. use of easily degradable chemicals in industry)

Control of Non-point source pollution:
Riparian buffers (nature based solution, NBS)

Riparian buffers significantly improves water quality through filtering pollutants

Also protects banks from erosion