7 Dissolved Oxygen

- Introduction
- Oxygen Saturation
- Biochemical Oxygen Demand
- Reaeration
- Streeter-Phelps Equation
- Nitrification
- Sediment Oxygen Demand
- Photosynthesis and Respiration
- Expanded Streeter-Phelps Equation
- Artificial Re-aeration

Dissolved Oxygen

- Important for aquatic health
  - DO standards typically 5 to 6 mg/L
- Redox chemistry
  - Affects release of chemicals bound to sediments
  - Anaerobic conditions => H_2S

Oxygen Saturation

$$
\begin{aligned}
c_s(T,S) = \exp\{&-1.3934411x10^2 + 1.575701x10^5/(T+273.15) \\
&-6.642308x10^7/(T+273.15)^2 + 1.243800x10^{10}/(T+273.15)^3 \\
&-8.621949x10^{11}/(T+273.15)^4 - S[1.7674x10^{-2} - 10.754/(T+273.15) \\
&+2.1407x10^3/(T+273.15)^2]\}
\end{aligned}
$$

$$c_s(T,S,p) = c_s(T,S)\left[\frac{(1-p_{wv}/p)(1-\theta p)}{(1-p_{wv})(1-\theta)}\right]$$

$$p_{wv} = \exp[11.8575 - 3.8407x10^3/(T+273.15) - 2.16961x10^5/(T+273.15)^2]$$

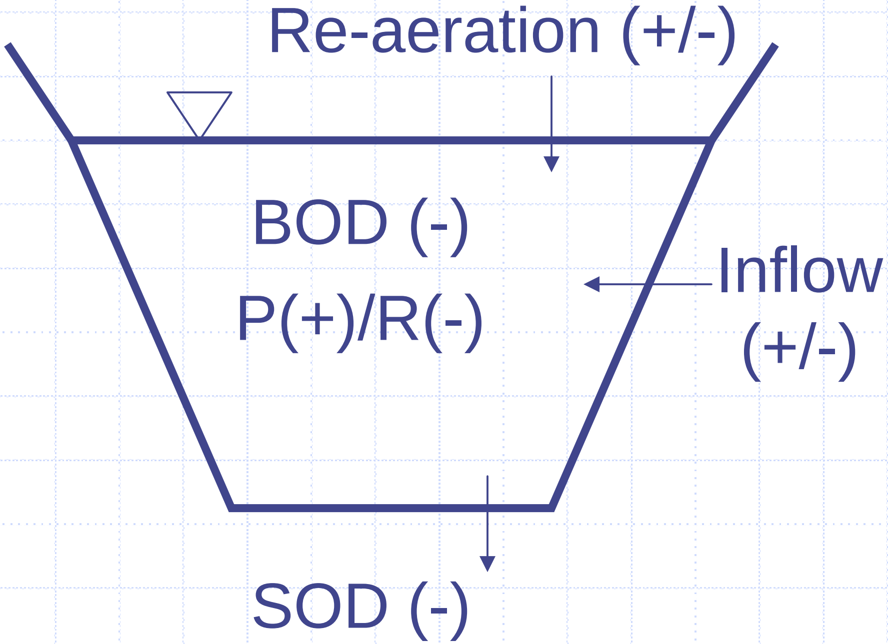
$$\theta = 0.000975 - 1.426x10^{-5}T + 6.436x10^{-8}T^2$$

Standard Methods (1995)

C_s (T, S, p)

	T=0°	10	20	30
Effect of p (S=0)				
p = 1 atm (z=0)	14.6	11.3	9.1	7.6
p = 0.89 (1000m)	12.9	19.9	8.0	6.7
p = 0.79 (2000m)	11.4	8.8	7.1	5.9
Effect of S (p=0)				
S = 0 PSU	14.6	11.3	9.1	7.7
S = 10	13.6	10.6	8.6	7.2
S = 35	11.4	9.0	7.4	6.2

Processes affecting DO



Re-aeration (+/-)

BOD (-)

P(+)/R(-)

Inflow (+/-)

SOD (-)

Biochemical Oxygen Demand

- Organic wastes are food for microorganisms
    - Oxygen consumed in process
    - Self-purification (bio-degradation) in natural waters
    - Biological stage of WWT
- Other chemicals exert oxygen demand
    - $C_2H_6O_2$
    - $NaHSO_3$

Theoretical Oxygen Demand

$$C_nH_aO_bN_cP_d + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3c}{4} + \frac{5d}{4}\right)O_2 = nCO_2 + \left(\frac{a}{2} - \frac{3c}{2} - \frac{3d}{2}\right)H_2O + cNH_3 + dH_3PO_4$$

Carbonaceous BOD (CBOD)

$$NH_3 + \frac{3}{2}O_2 = NO_2^- + H^+ + H_2O$$

$$NO_2^- + \frac{1}{2}O_2 = NO_3^-$$

Nitrogenous BOD (NBOD)

- Issues
  - Different types of wastes
  - Some not labile
  - Rates vary (nitrification)

Practical Measures of Oxygen Demand

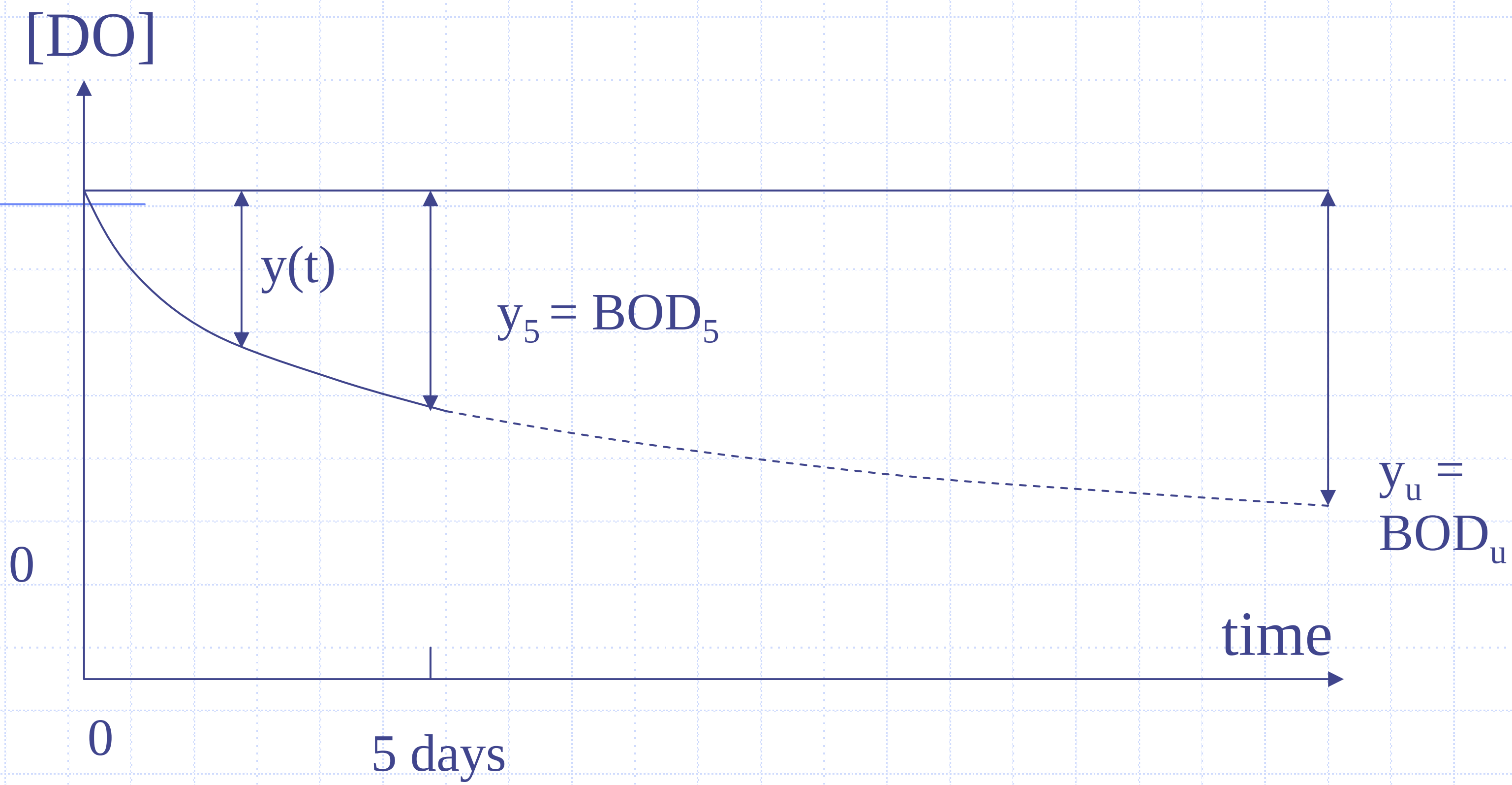
- BOD
  - Traditional water quality measure
  - Cumbersome and time-consuming
- COD
  - Easy to measure
- TOC
  - State variable in WQ models

Traditional BOD

- Practical measure of O_2 “debt”
  - How much DO would decrease due to respiration of organic wastes
- BOD Jar Test
  - Observe the decline of DO over time (e.g. 5 days)
  - Extrapolate to “ultimate” demand
  - Used for wastewater and natural waters

BOD Jar Test

- Precautions
  - No photosynthesis
  - Enough initial O_2
  - Adequate dilution (WW)
  - Enough microorganisms
  - Non toxic sample
  - Only carbonaceous BOD



$$y = L(1 - e^{-K_1 t})$$

$$L = \frac{L_5}{1 - e^{-5K_1}}$$

$$K_1 = K_1(20)\theta^{T-20}$$

$$K_1(20) \sim 0.1 - 0.5d^{-1}; \theta \sim 1.047$$

In rivers

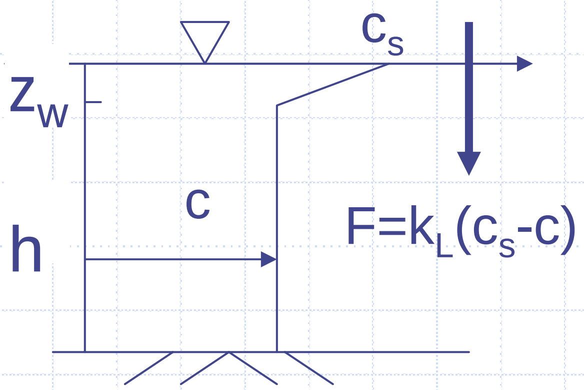
$$K_r = K_d + K_s$$

$$K_s = w_s / h$$

Other Measures of BOD

- COD
  - Easy to measure
  - Much quicker
- TOC
  - State variable in WQ models
- Relationship to BOD (Metcalf & Eddy)
  - BOD_5/COD ~ 0.4 to 0.8
  - BOD_5/TOC ~1.0 to 1.6

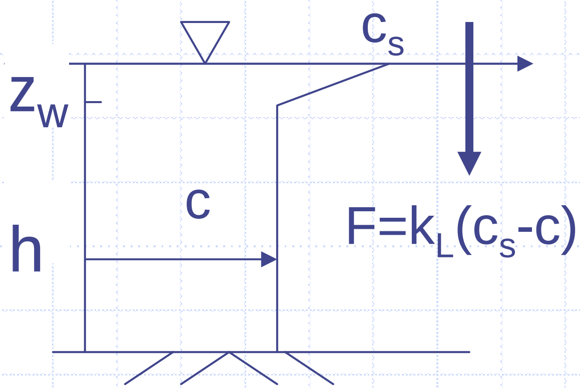
Stream Reaeration



$\delta = z_w$

- Water side control
- Flux F ~ DO deficit
- Piston velocity $[LT^{-1}]$
  - $k_L \sim k_w$
- Reaeration rate $[T^{-1}]$
  - $K_a = K_2 = k_w/h$
- Theories
  - Stagnant Film
  - Surface Renewal

Stream Reaeration



- Stagnant Film
    - $k_L = D/z_w$
- Surface Renewal
    - $z_w \sim (Dt)^{0.5}$
    - $t \sim h^2/E_z \sim h/u$
    - $z_w \sim (Dh/u)^{0.5}$
    - $k_L \sim (Du/h)^{0.5}$
    - $K_a \sim (Du/h^3)^{0.5}$

Stream Reaeration Formulae

- u in m/s, h in m, T=20º

$$K_a = \frac{3.93u^{0.5}}{h^{1.5}}$$

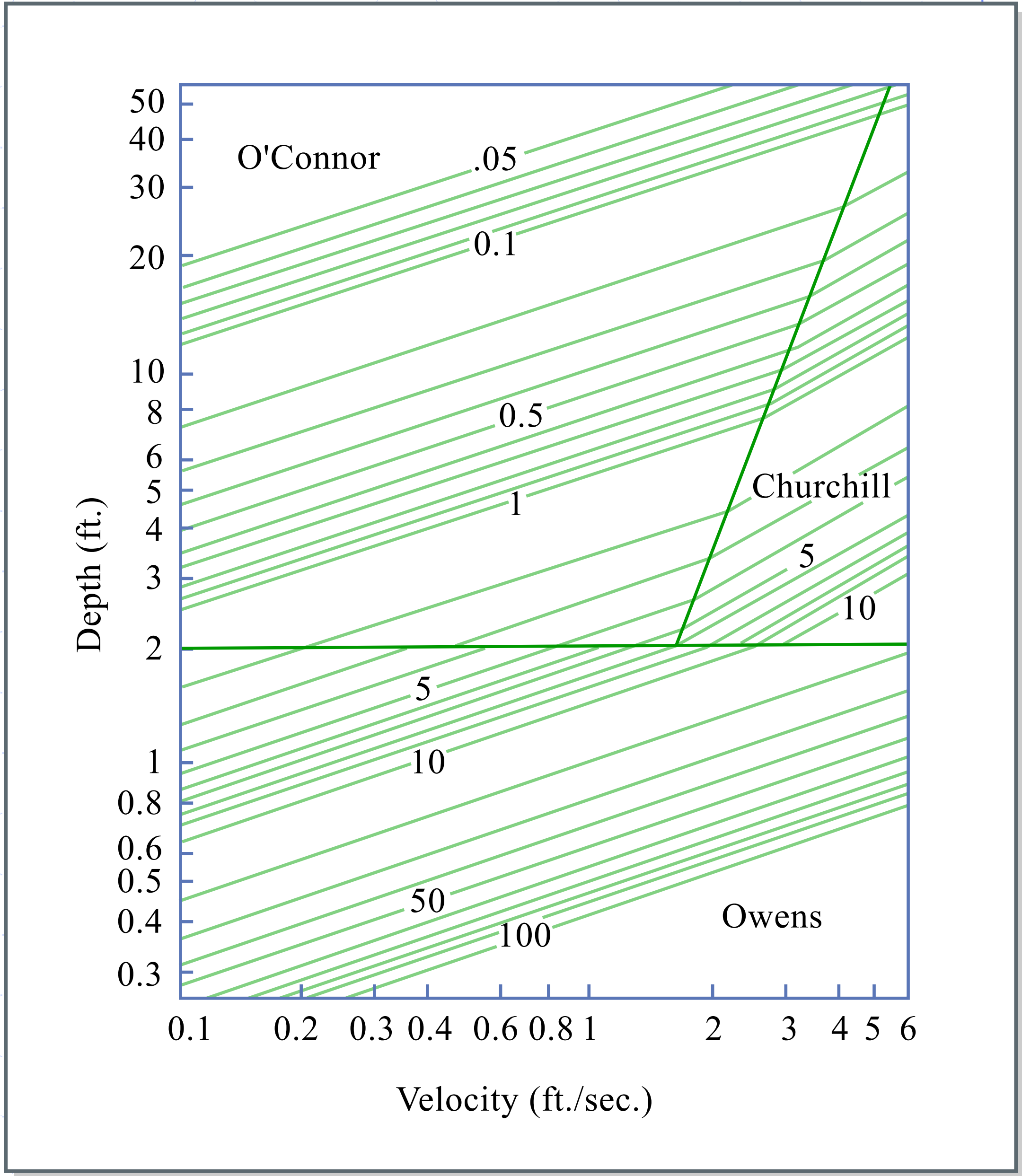
O'Connor-Dobbins (1958)

$$K_a = \frac{5.0u}{h^{1.67}}$$

Churchill et al. (1962

$$K_a = \frac{5.3u^{0.67}}{h^{1.85}}$$

Owens & Gibbs (1964)



Kovar, 1976

Figure by MIT OCW.

Other formulations

- Rate of Energy Dissipation (Tsivoglou & Wallace, 1972) $\frac{\Delta H}{T} = \frac{LS}{L/u} = uS$
- Melching and Flores (1999)

Pool and Riffle		Reaeration Coefficient K_a	CV
	$Q < 0.56$	$517(uS)^{0.524}Q^{-0.242}$	0.61
	$Q > 0.56$	$596(uS)^{0.528}Q^{-0.136}$	0.44
Channel Control			
	$Q < 0.56$	$88(uS)^{0.313}H^{-0.353}$	0.59
	$Q > 0.56$	$142(uS)^{0.333}H^{-0.66}W^{-0.243}$	0.60

1-D Analysis

(Streeter-Phelps, 1925)

Continuity

$$\frac{\partial A}{\partial t} + \frac{\partial}{\partial x}(Au) = q_\ell$$

Mass Transport

$$\cancel{\frac{\partial}{\partial t}(Ac)} + \frac{\partial}{\partial x}(Auc) = \cancel{\frac{\partial}{\partial x}(E_L A\frac{\partial c}{\partial x})} + A(r_i + r_e)$$

BOD (c = L)

$$r_i = -K_r L$$

$$r_e = q_\ell L_\ell / A$$

$$u\frac{dL}{dx} = -K_r L + \frac{q_\ell (L_\ell - L)}{A}$$

$$\tau = \int_0^x \frac{dx}{u(x)}$$

$$\frac{dL}{d\tau} = -K_r L + \nu (L_\ell - L)$$

$$L(\tau) = L_o \exp\left[-(K_r + \nu)\tau\right] + \frac{\nu L_\ell}{(K_r + \nu)}\left\{1 - \exp[-(K_r + \nu)\tau]\right\}$$

DO (c = c)

$$r_i = -K_d L$$

$$r_e = q_\ell c_\ell / A + K_a (c_s - c)$$

$$u \frac{dc}{dx} = -K_d L + K_a (c_s - c) + \frac{q_\ell (c_\ell - c)}{A}$$

$$\frac{dc}{d\tau} = -K_r L + K_a (c_s - c) + \nu (c_\ell - c) \qquad \Delta = c_s - c$$

$$\Delta(\tau) = \Delta_o \exp[-(K_a + \upsilon)\tau] + \frac{K_d \nu L_\ell}{(K_r + \nu)(K_a + \nu)} \{1 - \exp[-(K_a + \nu)\tau]\}$$

$$+ \frac{K_d}{(K_a - K_r)} \left[L_o - \frac{\nu L_\ell}{(K_r + \nu)} \right] \{\exp[-(K_r + \nu)\tau] - \exp[-(K_a + \nu)\tau]\}$$

Streeter-Phelps-additional comments

- c_{min} and x_{min} can be calculated analytically
- Multiple sources handled by superposition or re-initialization at stream confluences
- Procedures for anoxic conditions
- Neglect of longitudinal dispersion?
- Additional terms

Nitrification

$$C_nH_aO_bN_cP_d + (n + \frac{a}{4} - \frac{b}{2} - \frac{3c}{4} + \frac{5d}{4})O_2 = nCO_2 + (\frac{a}{2} - \frac{3c}{2} - \frac{3d}{2})H_2O + cNH_3$$
$$+ dH_3PO_4$$

$$NH_3 + \frac{3}{2}O_2 = NO_2^- + H^+ + H_2O$$

(2)(32/14) = 4.57

$$NO_2^- + \frac{1}{2}O_2 = NO_3^-$$

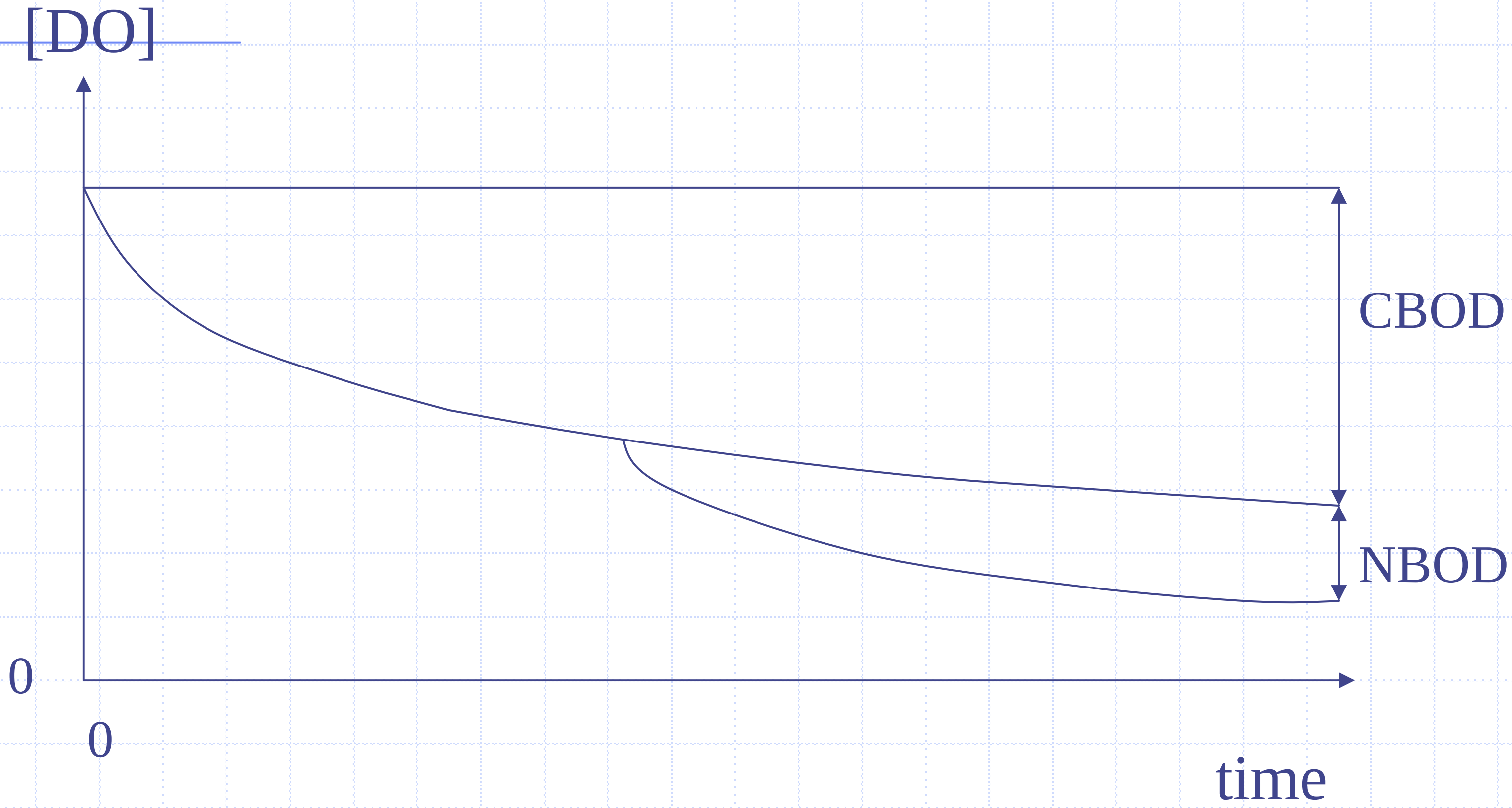
(0.5)(32/14) = 1.14

Theoretical (upper bound) NBOD

$$NBOD = 4.57(Org - N + NH_3 - N) + 1.14NO_2 - N$$

$$NBOD \cong 4.57TKN$$

TKN = total Kjeldalh nitrogen



Time scale for NBOD ~ 10 days => often insignificant in rivers

If important, separate CBOD & NBOD analyses required

May be better to include nitrogen species as state variables

Sediment Oxygen Demand (SOD)

- "BOD in sediments"
- Significant downstream from outfalls or following algal blooms
- $S_B = 0.1$ to $1\ g/m^2$-d
- $r_e = S_B/h$
  - O^{th} order process
  - 0.1 to 1 mg/L-d ($h = 1$ m)

SOD (cont'd)

- Measured
  - *in situ* with benthic flux chambers
  - in lab with core
- Calculated from organic carbon content of settled solids
- Calibrated from oxygen model
- Complication: extraneous sources

Benthic Flux Chambers

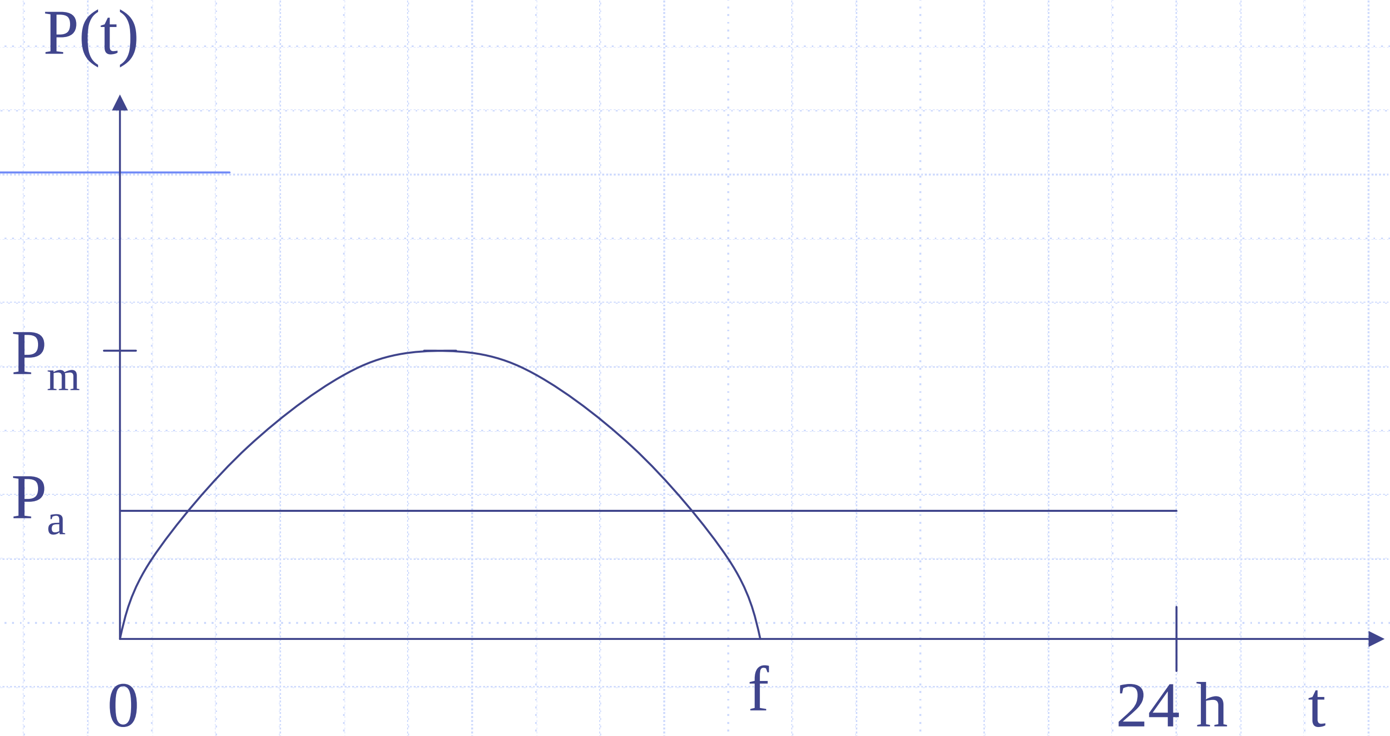
Zebra Mussels

Algal Photosynthesis and Respiration

- Photosynthesis (primary production) => fixation of CO_2 by autotrophic bacteria
- Reverse is respiration
- $6CO_2 + 6H_2O \Leftrightarrow C_6H_{12}O_6 + 6O_2$

P/R (cont’d)

- Limitations on primary production:
  - Light
  - Temperature
  - Nutrients
- Time and space dependent
  - Diurnal variation
  - Depth variation



$$P_a = \frac{2f}{24\pi} P_m$$

f = photoperiod (hrs)

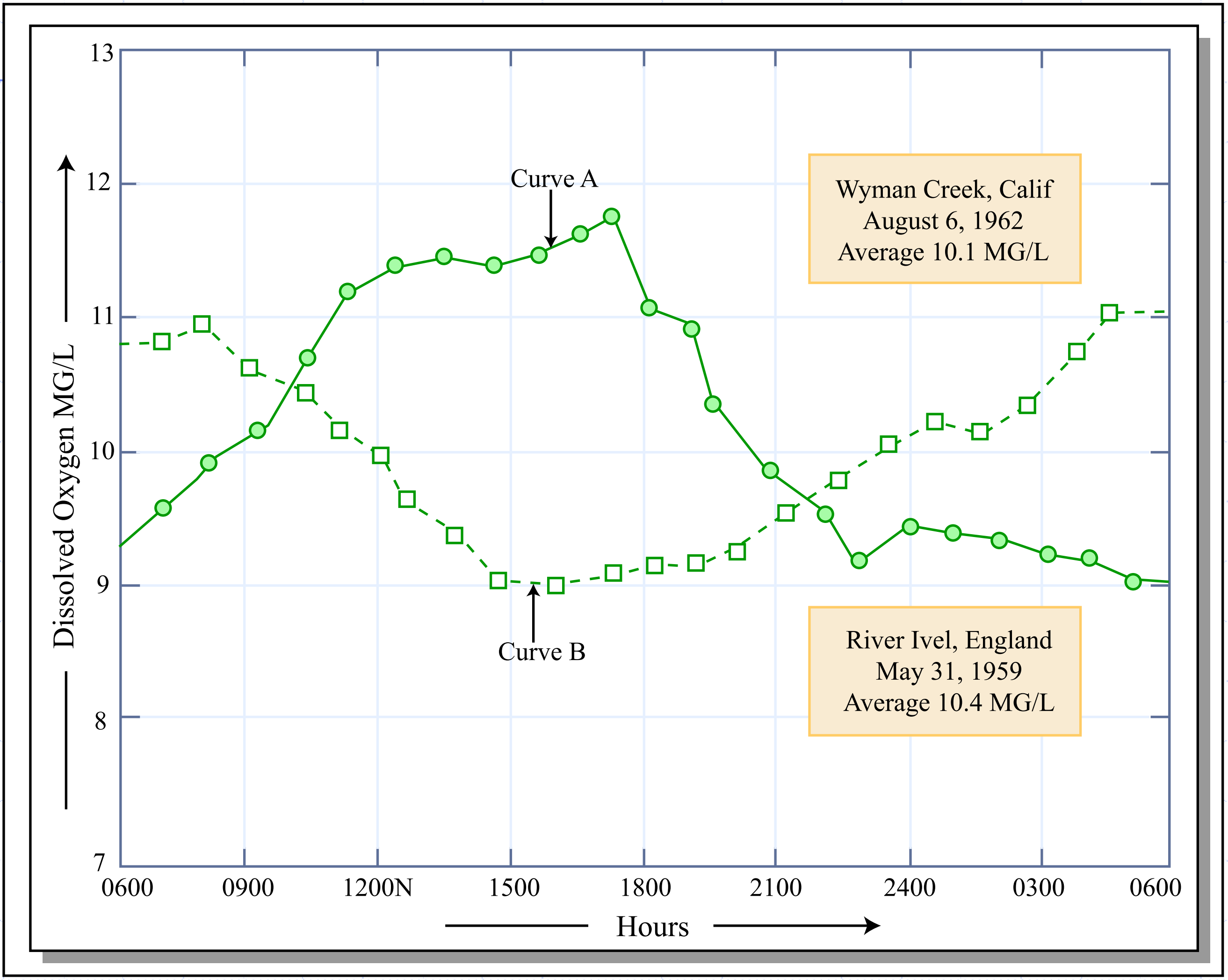


Figure by MIT OCW.

EPA (1985)

Estimation of P/R

- In situ measurements w/ Light & Dark Bottles

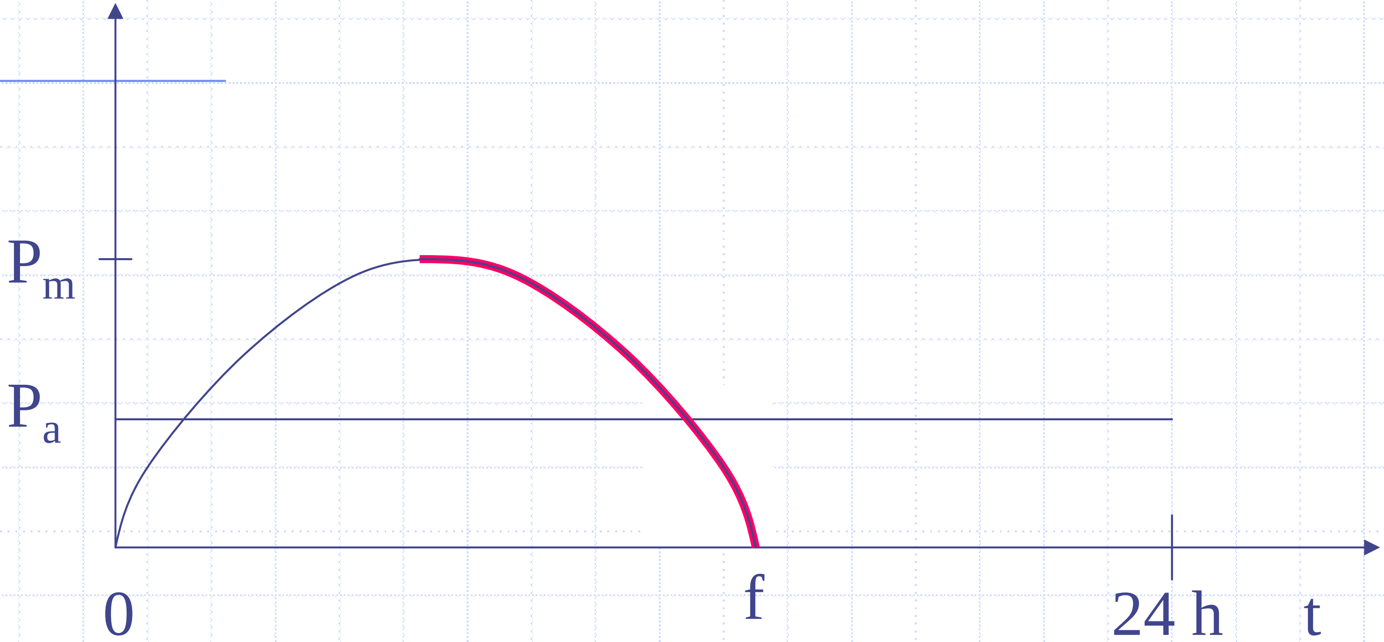
$$R = \left[\frac{c_o - c_t}{t}\right]_{dark} - K_d L$$

mg/L-d; L = ultimate BOD of filtered sample

$$P(t) = \left[\frac{c_t - c_o}{t}\right]_{light} - \left[\frac{c_t - c_o}{t}\right]_{dark}$$

P(t) is averaged over time t. t = 24 hrs => P_a;

t< 24 h => fit to diurnal variation using f


P_m
P_a
0
f
24 h
t

Estimation of P/R (cont'd)

- Calibrate to observed diurnal variation in P(t) using estimated K_a
  - "Delta" Method (Chapra and DiToro, 1979)
- Correlate with chlorophyll-a

$$P = 0.25 Chl - a$$

$$R = 0.025 Chl - a$$

Expanded Streeter-Phelps Eqs*

$$u\frac{dc}{d\tau} = -K_r L - K_N L_N + K_a (c_s - c) + \nu (c_\ell - c) - \frac{S_B}{h} + \frac{(P-R)}{h}$$

CBOD NBOD* Reaeration Lat Inflow SOD P/R

$$L(\tau) = L_o \exp\left[-(K_r + \nu)\tau\right] + \frac{\nu L_\ell}{(K_r + \nu)}\{1 - \exp[-(K_r + \nu)\tau]\}$$

$$L_N(\tau) = L_{No} \exp[-(K_N + \nu)\tau]$$

Expanded S-P (cont’d)

$$\Delta = \Delta_o \exp[-(K_a + \nu)\tau] +$$

$$\frac{K_d}{(K_a - K_r)}\left[L_o - \frac{\nu L_\ell}{K_r + \nu}\right]\{\exp[-(K_r + \nu)\tau] - \exp[-(K_a + \nu)\tau]\}$$

$$+\frac{K_d \nu L_\ell}{(K_r + \nu)(K_a + \nu)}\{1 - \exp[-(K_a + \nu)\tau]\}$$

$$+\frac{K_N L_{No}}{(K_a - K_N)}\{\exp[-(K_N + \nu)\tau] - \exp[-(K_a + \nu)\tau]\}$$

$$-\frac{(P - R - S_B / H)}{(K_a + \nu)}\{1 - \exp[-(K_a + \nu)\tau)]\}$$

Expanded S-P (cont’d)

Lateral BOD sources w/o significant inflow

$$L_{rd} = \frac{q_\ell L_\ell}{A} \qquad \upsilon = 0 \qquad \tau = x/u$$

$$\begin{aligned}
\Delta &= \Delta_o \exp(-K_a x/u) + \left\{ \frac{K_d L_o}{K_a - K_r} \left[\exp(-K_r x/u) - \exp(-K_a x/u) \right] \right\} \\
&+ \frac{K_N L_{No}}{(K_a - K_N)} \left\{ \exp(-K_N x/u) - \exp(-K_a x/u) \right\} \\
&+ \frac{K_d L_{rd}}{K_r K_a} \left[1 - \exp(-K_a x/u) \right] - \left\{ \frac{K_d L_{rd}}{(K_a - K_r) K_r} \right\} \left[\exp(-K_r x/u) - \exp(K_a x/u) \right] \\
&- \left(\frac{P - R - S_B / H}{K_a} \right) \left[1 - \exp(-K_a x/u) \right]
\end{aligned}$$

Artificial Reaeration

- Open water bodies (direct transfer, turnover, fountains)
- Hydropower stations (inject to turbine intake, downstream aeration)