Modeling in aquatic environment

Lecture 3

CSTR-models

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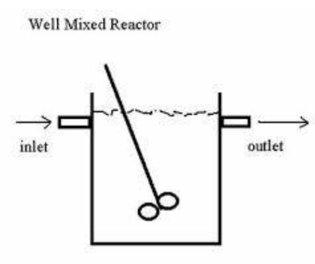
Completely stirred systems (CSTR)



- Inflows of pollutants must be known or estimated
- Processes (biological, chemical and physical) of pollutants in the lake must be known or estimated
  - – pollutant decay and reduction
  - – pollutant transformation
  - – pollutant release from sediments

Example of lake mass balance

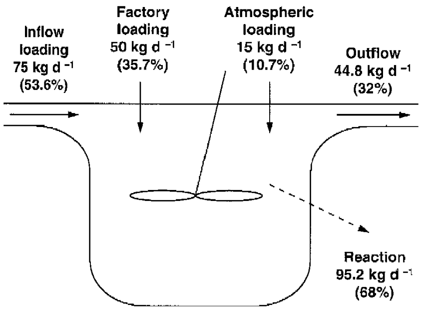


FIGURE 3.3
A mass balance for the well-mixed lake from Example 3.1. The arrows represent the major sources and sinks of the pollutant. The mass-transfer rates have also been included along with the percent of total mass inflow accounted for by each term.

Load input (W) to lake: mass balance basics

The load has as unit [mass/time]

$W = m/t$
W =load [dimension kg/a]
m = mass [kg]
t = time [d, a]
e.g. a paper mill discharges 100 kg of BOD and 1 kg P daily to the lake sewer treatment plan discharges W = 100 kg BOD/d or yearly W = 100 kg BOD * 365 / a = 3.65 t BOD/a

$W = Qc$
Q = discharge (m^3/s tai m^3/a)
c = concentration (kg/m^3), $c = m/V$, ja V = volume (m^3)
e.g. a sewer treatment plan discharges 1000 m^3/d at a concentration permit at maximum 0,3 mg P /l

$Q = UA_c$
U = stream flow/water velocity (m/s), the notation v also used
A_c = cross section area (m^2)
e.g. a river discharges 50 m^3/s of to water of P concentration 100 ug/l

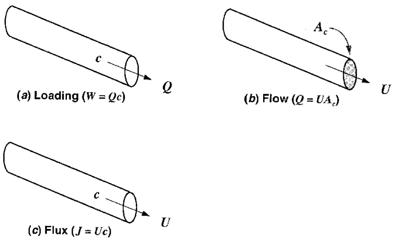
J =flux
$J= m/(tA_c)$

by replacing m with $m =Wt$
$J = W/ A_c$
from $W = Qc$ and $Q =U A_c$ we get $W = A_c Uc$

so
$J = U c$

unit dimensions e.g. g/m^2/d or m^3/m^2/d

e.g. an industrial fallout (air pollution) is 1 mg/m^2/d what is the load to the lake surface which is 1 km^2?



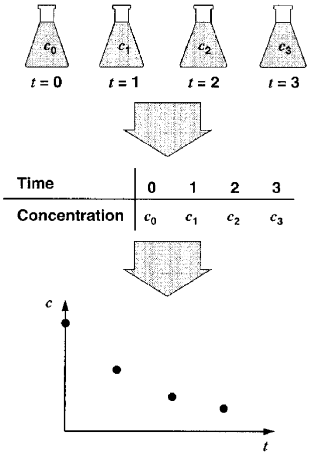
BOD=biological oxygen demand
BOD_7=amount of oxygen consumed. Measured during 7 days (kg or g)
Earlier BOD_5 was used

Reactions in lake:
phate of pollutants

- decay (biological, light, chemical)
- settling or sedimentation (physical process)
- biological uptake (e.g. algae) and sedimentation
- reactions in water producing new compounds (e.g. NH4 to NO3)
- reactions with the sediment

Reactions in lake:
how are they described mathematically?

- To study how a substance decays in water, let’s take a water sample (and keep it in constant temperature and stir it to keep fully mixed conditions and provide high oxygen availability) and measure how the concentration (c) changes in time (t).
- The change in concentration can then be plotted in a time-concentration diagram.
- After that a mathematical equation is fitted to these data points. This equation will give the required mathematical formulation describing the reactions.
- In general form this equation is $dc/dt = -kc^n$



Equations for pollutant decay

0 – order reaction, n = 0
$dc/dt = -kc^n$ or as n=0 $dc/dt = -k$
then $dc = -kdt$
with inegration this results in
$c = -kt + A$

From initial conditions
when t = 0 , then $c = c_0$ and $A = c_0$

$\mathbf{c = -kt + c_0}$

First oder reaction, n=1
$dc/dt = -kc^n$, $dc/dt = -kc$
$dc/c = -kdt$, with integration $lnc = -kt + A$
From initial conditions $t = 0$, $c = c_0$, $A = lnc_0$

$lnc – lnc_0 = -kt$
$ln(c/c_0) = -kt$
$c/c_0 = e^{-kt}$

$\boxed{\mathbf{c = c_0 e^{-kt}}}$

- The first order reaction is the most common equation used in environmental research and engineering (or engineering in general)
- The second order is also possible, e.g. in modelling of toxic substances
- The suitable order can be found by fitting these equations to the data and observing which eq. gives the best fit (or be comparing R^2-values)

Choice of model 0 or 1 order

- Plotting and inspection of data
- Curve fitting
- Parameter estimation
  - trial and error
  - least squares
- Goodness of fit
  - R^2 and its P-value

Parameter sensitivity k

How much does the relative pollutant concentration c/c_0 change, when k is changed?

For example k changed by 5 %

Change of pollutant mass in a lake

The mass balance requires that

the mass input – mass lost = mass change in the lake

Change in mass = $\Delta M/\Delta t$
using lake water concentration
as $c = M/V$ then $M=Vc$

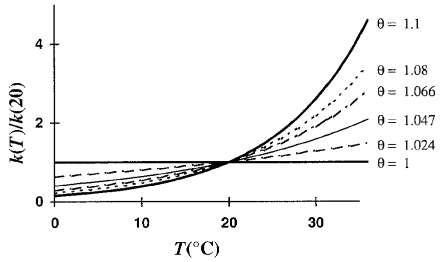
then $\Delta M/\Delta t = V\Delta c/\Delta t$ and assuming Δt to be small (differential)

Change in mass dM/dt = **Vdc/dt**

For removal by biological decay:
dM/dt = **-Vdc/dt**
1-order reaction
$dc/dt = -kc$
$dM/dt = -kM = -kVc$

k for the biological decay process depends on water temperature, BOD-concentration and type of wastewater

k (T) = k(20)θT-20



Wastewater type	k_r (20 °C)	BOD_5/BOD_{tot}	BOD_0(mg/l)
Raw sewer (untreated)	0,35 (0,2-0,5)	0,83	250
Primary treatment (sedimentation)	0,2 (0,1-0,3)	0,63	15-75
Chemical treatment	0,075 (0,05-0,10)	0,31	

Sedimentation (S)

mass removal by sedimentation

S=dM/dt = -vA

v = sedimentation velocity, fall velocity (m/d or m/s). First approximation from Stoke’s equation for spherical particles

A_s = lake area (sedimentation surface)

Inflow (W) and outflow of pollutants (O)

W = inflow of pollutants e.g. Qc_{in}

- Q discharge into the lake (e.g. m^3/d or m^3/s)

Outflow of pollutants O= Qc

- c = concentration in lake
- Q discharge out of the lake usually the same or larger than the inflow (depends on the water balance and lake catchment properties)

Mass balance equation for one lake

The required inflows, outflows and reactions of pollutants and grouped together and the equation results:

$$V\frac{dc}{dt} = W(t) - Qc - kVc - vA_Sc$$

change in lake mass = load input – load outflow – biol.decay - sedimentation

This equation is case dependent depending on the physical setting (flow patterns, number of lakes etc and the reactions recuried to solve the problem etc)

Simplification: No internal processes& steady state

$$\frac{dm}{dt} = W - O - S$$

- Where, m= total amount of phosphorus in a lake, W=total load of phosphorus entering to the lake, O=amount of phosphorus leaving the lake, S=retention (the amount of phosphorus (P) sediment to the lake)
- First applications by Piontelli and Tonolli (1969)
- In Vollenweiders (1969) solution the lake was considered as a continuously stirred tank (CSTR) and sedimentation of P was taken as following the first order kinetics with settling coefficient σ and phosphorus concentration (c) at the outlet was taken as mean concentration in the lake

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Vollenweider's equation

$$\frac{dm}{dt} = W - Qc - \sigma m$$

$$\rho = \frac{Q}{V} \Rightarrow \frac{dc}{dt} = \frac{W}{V} - \rho c - \sigma c$$

- Where, Q= water discharge at the outlet and ρ= exchange coefficient, σ=settling coefficient
- It is expected here that the lake volume is constant (eq. an annual mean)
- In steady state we mark phosphorus concentration as c_{ss} . It can be solved for time t

Solution for Vollenweider-equation

$$c = c_{ss} - (c_{ss} - c_0)e^{-(\rho+\sigma)(t-t_0)}$$

- Where c_0 is phosphorus concentration at time t_0
- Comments
  - Settling description with first order kinetics is too simple
  - Model can be used for studying the effects of loading options

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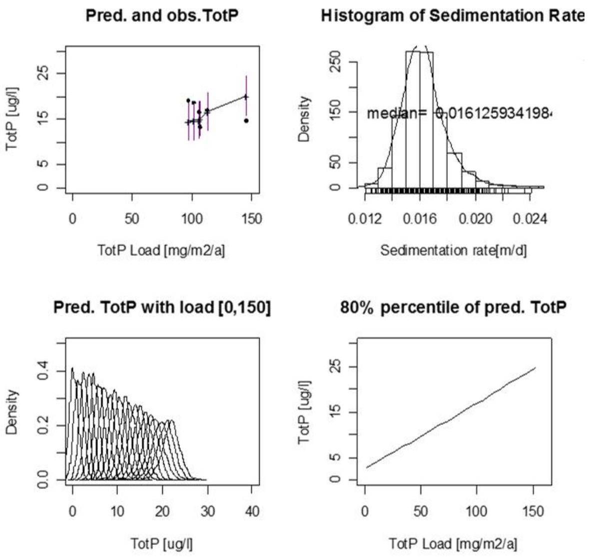
LLR-model /ToTP forecasts

Järven ravinnepitoisuus vs. ravinnekuormitus. Lasketut ja havaitut arvot



Estimoitu sedimentaatio nopeuden jakauma

TotP-jakauman ennusteet kuormituksilla [0,10,20, … ,150] kg/d

TotP-ennusteiden 80% fraktiili (20% ylitystodennäköisyys) kuormituksen funktiona

Examples of lake concentration with different pollution scenarios

- Example 1: Road salt runoff to different type of lakes
- Example 2: Nitrogen loading to a lake
- Example 3: Pesticide leaching to a lake
- Example 4: P load and limiting Nutrients

Example1: Road Salt

Road salting during winter months poses a threat to ecosystems and waters. Assuming that a road salt starts polluting the lake in 1900 with a load of 1000 kg/year. What is the concentration in the following lakes:

Lake 1: $V = 1\ 00\ 000\ m^3$, $Q = 1\ m^3/d$
Lake 2: $V = 1\ 000\ 000\ m^3$, $Q = 1\ m^3/d$
Lake 3: $V = 1\ 00\ 000\ m^3$, $Q = 10\ m^3/d$

$$V\frac{dc}{dt} = W(t) - Qc - kVc - vA_S c$$

W = 1000 kg/a = 2.74 kg/d

As the time is long since start of pollution, it can be assumed that the annual mean concentration does not change with time (constant). Therefore the term dc/dt=0. As the salt is conservative (not reactive) the reaction terms can be excluded. Therefore: 0 = W –Qc or W = Qc and c=W/Q and the concentrations in the lakes are

lake 1: c =W/Q = 2.74 kg/m^3 = 2.74 1000g/1000l =**2.74 g/l**
lake 2: c = W/Q = 2.74 kg/m3 = 2.74 1000g/1000l =**2.74 g/l**
lake 3: c = W/Q = 0.274 kg/m3 = 0.274 1000g/1000l =0.274 1000 000 mg/l =**274 mg/l**

It can be seen that the lake **steady state** concentration depends on the inflow discharge of water and not the lake volume. In this case the lake is not sensitive to lake volume V changes.

Example 2 Nitrogen loading to a lake

Nitrogen is easily leached from agricultural areas as a result of fertilizer application. Also municipal wastewater contribute to nitrogen loads. Assuming that dissolved nitrogen starts polluting the lake in 1900's (wastewater treatment plant) with a load of 1000 kg/year. What is the concentration in the following lakes:

Lake 1: V = 1 00 000 m^3, Q = 1 m^3/d
Lake 2: V = 1 000 000 m^3, Q = 1 m^3/d
Lake 3: V = 1 00 000 m^3, Q = 10 m^3/d

W = 1000 kg/a = 2.74 kg/d

As the time is long since start of pollution, it can be assumed that the annual mean concentration does not change with time (constant). Therefore the term dc/dt=0. Based on literature, the nitrogen decay constant k can be assumed to be 7 1/a which is 0.02 1/d. http://www.ncbi.nlm.nih.gov/pubmed/17802850

Therefore: 0 = W –Qc- kcV and then c=W/(Q+kV) and the concentrations in the lakes are

lake 1: c =W/(Q+kV) = 2.74 kg/d **/**(1 m3/d + 0.021/d* 1 00 000 m^3) =0.001369 kg/m3 =1,37 mg/l
lake 2: c = W/(Q+kV) = 0.137 mg/l
lake 3: c = W/(Q+kV) = 1.36 mg/l

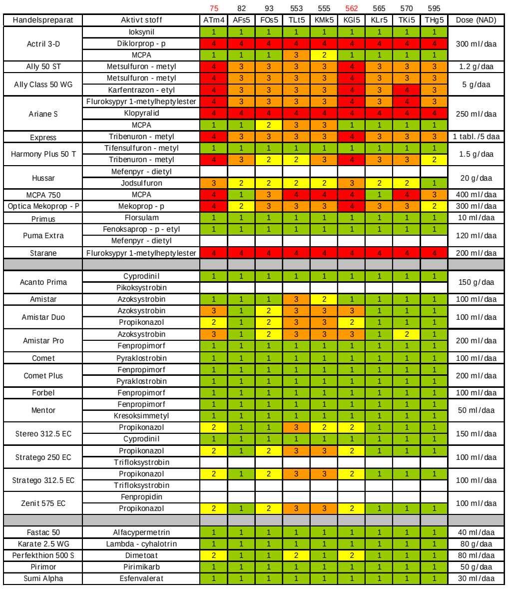
It can be seen that the lake **steady state** concentration depends on the inflow discharge of water and the lake volume. The concentration is sensitive to changes in lake volume.

Example 3: Pesticide leaching to a lake

Pesticides are widely used in agriculture and also in traffic (road and railroads) to control weed and pests. They are strongly absorbed to soils and only part of the toxic will leach with runoff water from agricultural areas. The leaching risk depends on

- The type of pesticide
- The adsorption to the soil
- The soil type

Leaching pose a major environmental risk to humans and ecosystems as these substances are toxic.



Brand and chemical soil classification type

		75	82	93	553	555	562	565	570	595	
Handelspreparat	Aktivt stoff	ATm4	AFs5	FOs5	TLt5	KMk5	KGl5	KLr5	TKi5	THg5	Dose (NAD)
Actril 3-D	Ioksynil	1	1	1	1	1	1	1	1	1	300 ml/daa
	Diklorprop - p	4	4	4	4	4	4	4	4	4	
	MCPA	1	1	1	3	2	1	1	1	1	
Ally 50 ST	Metsulfuron - metyl	4	3	3	3	3	4	3	3	3	1.2 g/daa
Ally Class 50 WG	Metsulfuron - metyl	4	3	3	3	3	4	3	3	3	5 g/daa
	Karfentrazon - etyl	4	3	3	3	3	4	3	4	3	
Ariane S	Fluroksypyr 1-metylheptylester	4	3	3	3	3	4	3	4	3	250 ml/daa
	Klopyralid	4	4	4	4	4	4	4	4	4	
	MCPA	1	1	2	3	3	1	1	1	1	
Express	Tribenuron - metyl	4	3	3	3	3	4	3	3	3	1 tabl. /5 daa
Harmony Plus 50 T	Tifensulfuron - metyl	1	1	1	1	1	1	1	1	1	1.5 g/daa
	Tribenuron - metyl	4	3	2	2	3	4	3	3	2	
Hussar	Mefenpyr - dietyl										20 g/daa
	Jodsulfuron	3	2	2	2	2	3	2	2	1	
MCPA 750	MCPA	4	1	3	4	4	4	1	4	3	400 ml/daa
Optica Mekoprop - P	Mekoprop - p	4	2	3	3	3	4	3	3	2	300 ml/daa
Primus	Florsulam	1	1	1	1	1	1	1	1	1	10 ml/daa
Puma Extra	Fenoksaprop - p - etyl	1	1	1	1	1	1	1	1	1	120 ml/daa
	Mefenpyr - dietyl										
Starane	Fluroksypyr 1-metylheptylester	4	4	4	4	4	4	4	4	4	200 ml/daa
Acanto Prima	Cyprodinil	1	1	1	1	1	1	1	1	1	150 g/daa
	Pikoksystrobin										
Amistar	Azoksystrobin	1	1	1	3	2	1	1	1	1	100 ml/daa
Amistar Duo	Azoksystrobin	3	1	2	3	3	3	1	1	1	100 ml/daa
	Propikonazol	2	1	2	3	3	2	1	1	1	
Amistar Pro	Azoksystrobin	3	1	2	3	3	3	1	2	1	200 ml/daa
	Fenpropimorf	1	1	1	1	1	1	1	1	1	
Comet	Pyraklostrobin	1	1	1	1	1	1	1	1	1	100 ml/daa
Comet Plus	Fenpropimorf	1	1	1	1	1	1	1	1	1	200 ml/daa
	Pyraklostrobin	1	1	1	1	1	1	1	1	1	
Forbel	Fenpropimorf	1	1	1	1	1	1	1	1	1	100 ml/daa
Mentor	Fenpropimorf	1	1	1	1	1	1	1	1	1	50 ml/daa
	Kresoksimmetyl	1	1	1	1	1	1	1	1	1	
Stereo 312.5 EC	Propikonazol	2	1	1	3	2	2	1	1	1	150 ml/daa
	Cyprodinil	1	1	1	1	1	1	1	1	1	
Stratego 250 EC	Propikonazol	2	1	2	3	3	2	1	1	1	100 ml/daa
	Trifloksystrobin										
Stratego 312.5 EC	Propikonazol	2	1	2	3	3	2	1	1	1	100 ml/daa
	Trifloksystrobin										
Zenit 575 EC	Fenpropidin										100 ml/daa
	Propikonazol	2	1	2	3	3	2	1	1	1	
Fastac 50	Alfacypermetrin	1	1	1	1	1	1	1	1	1	40 ml/daa
Karate 2.5 WG	Lambda - cyhalotrin	1	1	1	1	1	1	1	1	1	80 g/daa
Perfekthion 500 S	Dimetoat	2	1	1	2	1	2	1	1	1	80 ml/daa
Pirimor	Pirimikarb	1	1	1	1	1	1	1	1	1	50 g/daa
Sumi Alpha	Esfenvalerat	1	1	1	1	1	1	1	1	1	30 ml/daa

1 = ingen risiko
2 = lav risiko
3 = moderat risiko
4 = høy risiko

increasing level of risk

Pesticide leaching

- Assuming that pesticides/herbicides starts polluting the lake in 1960's (nearby railroad where this is used) with a load of 10 kg/year. What is the concentration in the following lakes:

- Lake 1: V = 1 000 00 m3, Q = 1 m3/d
- Lake 2: V = 1 000 000 m3, Q = 1 m3/d
- Lake 3: V = 1 000 00 m3, Q = 10 m3/d

- W = 1000 kg/a = 2.74 kg/d

- As the time is long since start of pollution, it can be assumed that the annual mean concentration does not change with time (constant). Therefore the term dc/dt=0. Pesticides consist of many groups of chemicals. We assume here that the k value is 0.02 1/d. see chan and chu WR 2005.

- lake 1: c =W/(Q+kV) = 2.74 kg/d /(1 m3/d + 0.021/d* 1 00 000 m3) =0.001369 kg/m3 =1,37 mg/l
- lake 2: c = W/(Q+kV) = 0.137 mg/l
- lake 3: c = W/(Q+kV) = 1.36 mg/l

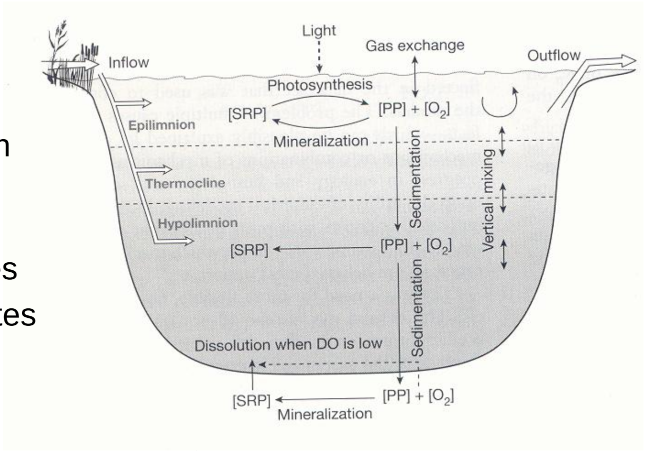
- It can be seen that the lake **steady state** concentration depends on the inflow discharge of water and the lake volume.

Example 4: P load and limiting Nutrients

- Most freshwater ecosystems are *phosphorus limited*
- Inputs of the limiting nutrient will result in a biological productivity increase – growth of algae- eutrophication
- Most marine systems are *nitrogen limited*
- Excessive inputs will cause an *algal bloom*
- It estimated that total phosphorus concentration in lake water should be below 0.010-0.015 mg/L to prevent algal blooms

Lake Chemistry - Phosphorus

- P limits biological production in lakes
- In figure: P cycle in lakes
- P accumulates in the sediments



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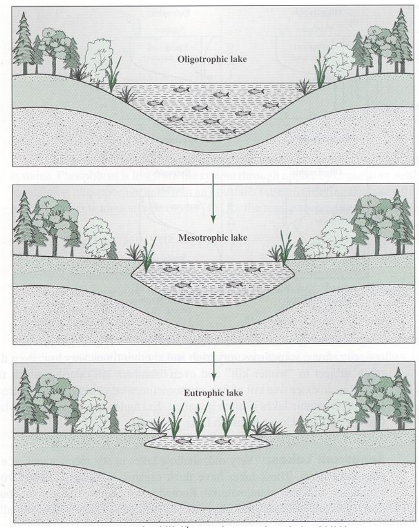
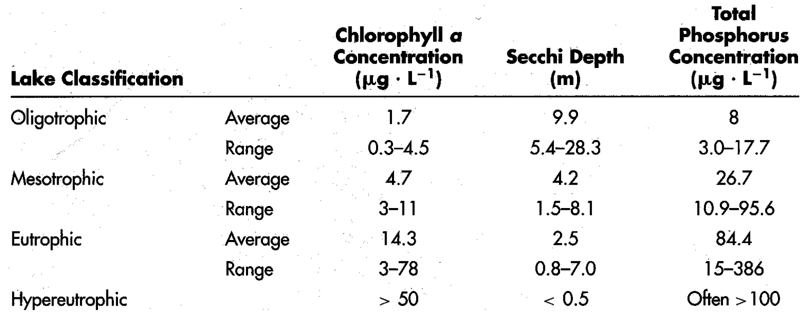
Lake Succession or Eutrophication



Perspective on Eutrophication

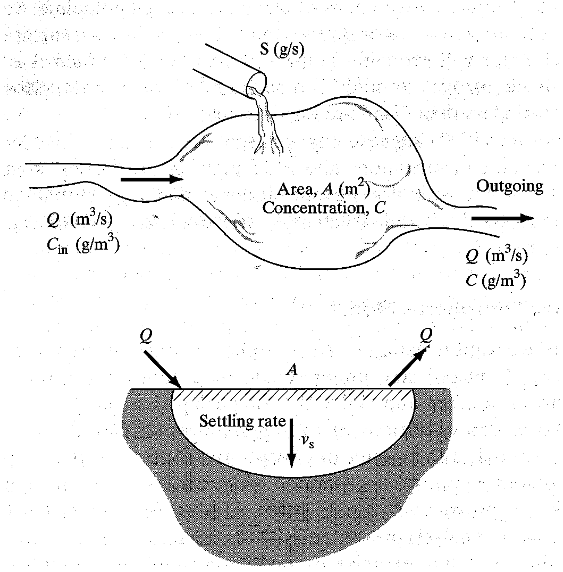
- Eutrophication is a natural process
- Some lakes have been eutrophic long before human activities could have had any effect
- Aging process is thought to occur over thousands of years
- *Cultural eutrophication* is accelerated aging due to human influences
- May occur over tens of years

Lake Classification



Lake Classification		**Chlorophyll *a* Concentration** $(\mu g \cdot L^{-1})$	**Secchi Depth (m)**	**Total Phosphorus Concentration** $(\mu g \cdot L^{-1})$
Oligotrophic	Average	1.7	9.9	8
	Range	0.3–4.5	5.4–28.3	3.0–17.7
Mesotrophic	Average	4.7	4.2	26.7
	Range	3–11	1.5–8.1	10.9–95.6
Eutrophic	Average	14.3	2.5	84.4
	Range	3–78	0.8–7.0	15–386
Hypereutrophic		> 50	< 0.5	Often > 100

A Simple Phosphorus Model



A Simple Phosphorus Model

$$\text{accumulation} = \text{input - output} \pm \text{reaction}$$

$$V\frac{dP}{dt} = QP_{in} + S - QP - k_s VP$$

S = loading from point source (g/s)

P = P concentration in lake (g/m^3)

P_{in}= P concentration in incoming stream (g/m^3)

Q = stream inflow and outflow (m^3/s)

k_s = P removal rate (1/s)

A = surface area of the lake (m^2)

V = volume of the lake (m^3)

A Simple Phosphorus Model

- Solution (steady state)

$$P = \frac{QP_{in} + S}{Q + k_s V}$$

- The removal rate is empirical (not based on theory). A common method for describing removal is to use settling rate or velocity – still empirical but more consistent with mechanism and more uniform
- Reaction term is $v_s A\ P = k_s V P$

Example

- A phosphorus limited lake with a volume of 8 x 10^8 m^3 is fed by a 15 m^3/s stream with a P concentration of 0.010 mg/L.
  - Estimate the total steady-state P concentration in the lake
  - How would you classify the lake?
  - What level of P removal would be required in the point source to keep the P level below 0.015 mg/L? So we need to solve the value for S

Example

All units are consistent, except the removal rate

$$k\left(\frac{1}{\text{yr}}\right)\left(\frac{1}{60}\frac{\text{min}}{\text{s}}\right)\left(\frac{1}{60}\frac{\text{hr}}{\text{min}}\right)\left(\frac{1}{24}\frac{\text{d}}{\text{hr}}\right)\left(\frac{1}{365}\frac{\text{yr}}{\text{d}}\right)=3.2\times10^{-8}\frac{1}{\text{s}}$$

Calculate the steady - state concentration

$$P=\frac{QP_{in}+S}{Q+k_sV}$$

$$P=\left(\frac{\left(15\frac{\text{m}^3}{\text{s}}\right)\left(0.010\frac{\text{g}}{\text{m}^3}\right)+1\frac{\text{g}}{\text{s}}}{15\frac{\text{m}^3}{\text{s}}+\left(3.2\times10^{-8}\frac{1}{\text{s}}\right)\left(8\times10^{8}\ \text{m}^3\right)}\right)=0.028\frac{\text{g}}{\text{m}^3}$$

Example

- According to Table on slide 29, a P-concentration of 0.028 g/m^3 = 28 µg/L would indicate a classification of <u>mesotrophic</u>
- Rearranging, and solving S, when P = 0.015 g/m^3 we get:

$$S=Q(P-P_{in})+k_sVP$$

$$S=15\frac{\text{m}^3}{\text{s}}\left((0.015-0.010)\frac{\text{g}}{\text{m}^3}\right)$$
$$+\left(3.2\times10^{-8}\frac{1}{\text{s}}\right)\left(8\times10^{8}\ \text{m}^3\right)\left(0.015\frac{\text{g}}{\text{m}^3}\right)=0.46\frac{g}{s}$$

Forming mass balance equations

- The equation depends on the water system modelled and on processes involved
  - One lake, two lakes etc
  - Pollutants that decay, conservative, or pollutants that settle (sedimentation)

When is the completely mixed (CSTR) approach for lakes applicable?

- When the lake is completely mixed
  - shallow lakes or non-stratified lakes
- When the residence time is sufficient
- When data is only available for simple approaches
- When time limits other calculations
- The complete mixed model approach is widely used!