Water properties

Pathogens

Dissolved Oxygen

(Water Quality)

Pollution affects water use; Water use affects water (Pollution) quality.

Water has multiple uses; drinking, agricultural (consumptive), industrial, ecological, etc.

Water has special properties; dipole moment (at molecular level a water molecule has a ⊕ end and a ⊖ end) - explains many of the unusual physical & thermodynamic properties of H_2O.

density decreases with decreasing T near liquid-solid phase change - ice floats; ρ_{max} at 4°C; liquid stratifies, warm water floa

high MP & BP for its molecular weight. Its triple point exists at typical terrestrial temperatures.

high heat capacity and high heat of vaporization; helps absorb energy and moderate temperature change globally

"Universal solvent" - both polar & non-polar compounds dissolve to some extent in water. Thus it serves as a medium for nutrient & waste transport in living systems.

Water vapor absorbs (and re-emits) infrared radiant energy; greenhouse effect, helps keep earth habitable.

Hydrologic Cycle

Nearly all exploitable water exists in the hydrologic cycle

~96% oceanic * (See Table 5.1)

~2% ice & glaciers

~2% groundwater } available for consumption

0.01% surface water (fresh) }

*can use RO to consume seawater but currently very costly!

Total proven water reserves ~ $23.5 \cdot 10^{15}\ m^3$

USA usage $403 \cdot 10^6\ m^3/d$ (consumptive use) (See Table 5.1)

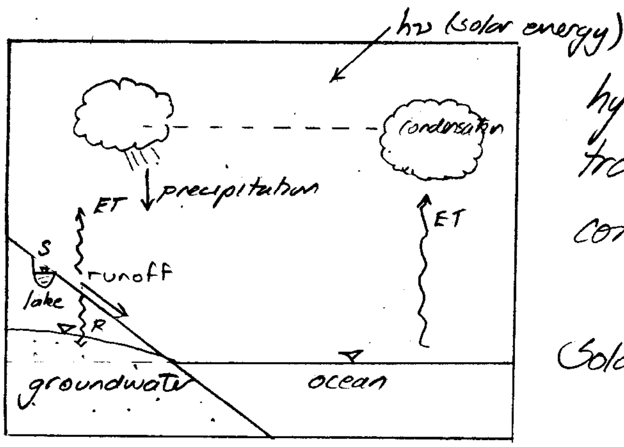
~ $1.7 \cdot 10^{-6}\ \%/d$ of reserves is in use in USA

Only a small fraction of the reserves are economically exploitable

Water balance

Withdrawl = Consumption + Return. (See Fig 5.5)

Consumption: Water becomes unavailable for near-future use (evaporation), or water is removed from hydrologic cycle (deep-well injection)



hydrologic cycle refers to cyclic transport of water into different compartments in the hydrosphere.

Solar (thermal) energy drives system

Engineering concerns/challenges; water supply; flood protection; waste discharge; ecological (quality & quantity) protection; disease control

Pollutants

Materials that render water unfit for intended use.

Pollutants

pathogens - disease
O_2 demanding wastes - ecosystem; waste assimilation
nutrients - ecosystem
salts - ecosystem; agriculture
thermal pollution - ecosystem
metals - toxic; ecosystem & human health
pesticides - ecosystem
volatile organics - toxic; ecosystem & human health

Pathogens - organisms that cause disease
bacteria, protozoa, parasites, virus, prion
water borne - cholera, typhoid; watershed - lack of water for hygene
water based - schistosomiasis (contact); water related - malaria, dengue, SLE.
In the developed nations pathogens are controlled by
disinfection (bacteria, protozoa, some parasites); filtration (parasites & virus);
inspection (bacteria, virus, prion).
Undeveloped nations best hope is point-of-use disinfection.
In USA fecal coliform is measured as an indicator of pathogen potential in water

O_2 demanding wastes

DO is an important feature of water quality. Fish & other organisms need O_2 to live; otherwise only anaerobic organisms will survive. Important equilibria depend on O_2 in water - esp. toxic metals.

O_2 demanding wastes - materials whose presence & degradation uses O_2 and reduces DO in water.

DO is a measure of O_2 in water.

BOD, COD are measures that indicate the oxygen demand of a waste stream.

Nutrients

Materials essential to life. Pollutants because stimulate growth that exceedes carrying capacity of the system and eventually destroys the ecosystem.

Nitrogen (N) & Phosphorous (P; PO_4) are usually the limiting nutrients in natural systems. Most control focuses on these species.

Nutrient enrichment accelerates natural eutrophication.

N compounds (NO_3) are toxic to infants. P is quite limited in natural systems - modern civilization has greatly changed P (increased) in ecosystem.

Salts

Have significant impact on agriculture.

High conc. can make water unsafe to drink. RO & similar technologies can remove salt, but are energy intensive (i.e. not economical for Ag)

Thermal pollution

$DO_{sat} \downarrow$ as temperature $\uparrow$; Aquatic diversity $\downarrow$ as temp $\uparrow$.

Metals

Most metals are toxic depending on oxidization state. Some are essential trace nutrients, but toxic in large amounts. DO & pH play big role in metal availability - usually low DO & low pH are problematic with regards to metal.

Pesticides

Organophosphates
carbamates } endocrine disrupters; cholinesterase inhibitors

$\underbrace{\text{endocrine disrupters}}_{\text{impact reproduction \& immune system}}$; $\underbrace{\text{cholinesterase inhibitors}}_{\text{nerve agents}}$

chlorinated hydrocarbons (herbicides) – carcinogens; immune system.

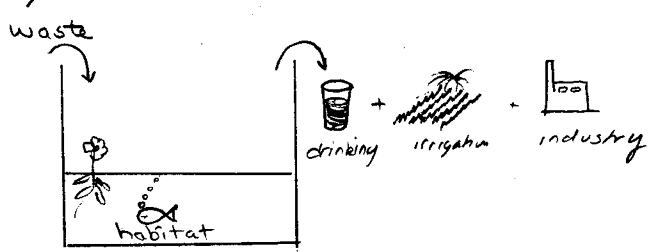
Volatile organic compounds (VOC)

Used as solvents & fuels. Carcinogen & mutagens.
Extremely common in contaminated groundwater. Some are very toxic at low doses.

Dissolved Oxygen and O_2 Demand

Surface water systems are used for
drinking water, agriculture, aquatic habitat (fish consumption; shellfish consumption), contact recreation, and waste assimilation.

can group into three distinct uses/needs
water supply, waste assimilation (disposal), aquatic habitat



aquatic life needs a certain level of DO to survive.
wastes are metabolized by microorganisms – this metabolism uses O_2.

(1) organic + $\underset{\approx}{O_2}$ $\xrightarrow{\text{microorganisms}}$ $CO_2 + H_2O$ + more cells + by products ($NO_3, PO_4, SO_4 \cdots$)

aerobic

(2) organic + $\approx$ $\xrightarrow{\text{microorganisms}}$ $CO_2 + H_2O$ + more cells + by products (NH_3, H_2S, $CH_4 \cdots$)

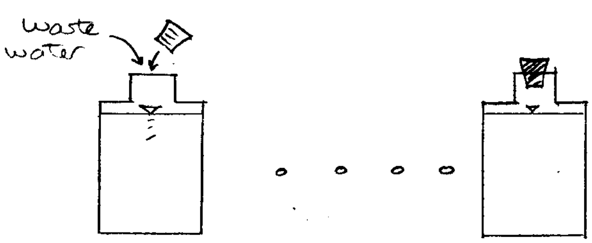
anaerobic

amount of O_2 required in path (1) to oxidize all the waste is called the biochemical oxygen demand (BOD).
Comprised of two parts: CBOD (carbonaceous); NBOD (nitrogeneous)

5-day BOD test

Ideally one would measure all O_2 required to oxidize waste – takes too long. In practice only part of time required is used. Typically a 5-day interval is used.

BOD_5 is a common test



t=0, measure DO   t=5 day, measure DO

mass O_2 initially:
$= \forall DO_0$

mass O_2 final
$= \forall DO_5$

Mass balance on DO.

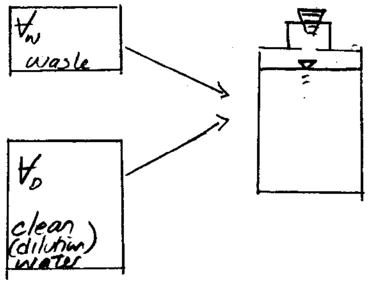
$$\Delta \text{Mass } O_2 = \text{Mass Initial} - \text{mass final}$$

$$= \forall DO_0 - \forall DO_5$$

$$BOD_5 = \frac{\Delta \text{Mass } O_2}{\text{Volume}} = \frac{\forall DO_0 - \forall DO_5}{\forall}$$

$$= DO_0 - DO_5$$

Usually waste has very high BOD, so only a small fraction of waste is added & remainder is clean water.



$$\frac{(V_W + V_D)DO_0 - (V_W + V_D)DO_5}{V_W} = \frac{\text{mass } O_2 \text{ initial} - \text{mass } O_2 \text{ final}}{\text{Volume waste}} = BOD$$

$$\therefore \quad BOD_5 = DO_0 - DO_5 \underbrace{\frac{(V_W + V_D)}{V_W}}_{\frac{1}{P}\text{; } P = \text{dilution factor}} = \frac{DO_0 - DO_5}{P}$$

Standard BOD bottles are 300mL, so P is usually $\frac{V_{waste}}{300mL}$

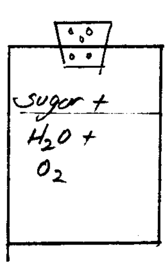
Important concepts:

<u>BOD</u> is a <u>measurement</u> that indicates relative oxygen demand of a (waste) water.

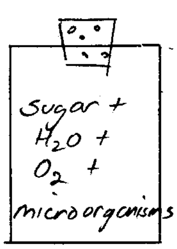
<u>BOD</u> is usually reported in concentration units (mg/L).

<u>BOD</u> is not a chemical, compound, or organism – it is an observed responce to presence of materials that are degraded by organisms.

$\therefore$ "A water has a BOD value of y mg/L" is a correct statement. "The concentration of BOD in the water ..." is incorrect.



BOD = ? (0)



BOD = ? (>0)

} important distinction – need microorganisms to have BOD.

Example 10 mL sewage + 290 mL water. $DO_0 = 9\,mg/L$

Desire at least 2 mg/L drop in DO during test. For what range of BOD_5 is this dilution useful? Minimum final DO > 2 mg/L

$P = \frac{10}{300} = \frac{1}{30}$ $\quad \Delta DO_{min} = 2\,mg/L \quad \Delta DO_{max} = 7\,mg/L$

$$\therefore \quad BOD_5 = \frac{9\,mg/L - 2\,mg/L}{P} = \frac{7(30)}{(1)} = 210\,mg/L$$

$$BOD_5 = \frac{9 - 7\,mg/L}{P} = \frac{2(30)}{1} = 60\,mg/L$$

$\therefore$ This dilution will be useful for BOD_5 ranging from 60–210 mg/L.

Typically dilution water exherts its own BOD, so a blank is conducted also.

V_c

Control

$$BOD_c(V_c) = BOD_d(V_d) \text{ but } BOD_c = BOD_d \text{ because use same source water.}$$

$V_d + V_w$

mixture

$$BOD_T(V_D + V_w) = BOD_w V_w + BOD_D V_D$$

$$BOD_T(V_D + V_w) - BOD_D V_D = BOD_w V_w$$

$$BOD_T \frac{V_D}{V_w} + BOD_T \frac{V_w}{V_w} - BOD_D \frac{V_D}{V_w} = BOD_w$$

$$BOD_T \underbrace{\left(\frac{V_D + V_w}{V_w}\right)}_{=\frac{1}{P}} - BOD_D \underbrace{\left(\frac{V_D}{V_w}\right)}_{\frac{1}{P} - 1} = BOD_w$$

$$\therefore BOD_T\left(\frac{1}{P}\right) - BOD_D\left(\frac{1}{P} - \frac{P}{P}\right) = BOD_w$$

$$\longrightarrow \quad BOD_w = \frac{(DO_0 - DO_5)_{mixture} - (DO_0 - DO_5)_{control}(1-P)}{P}$$

BOD as a 1^{st} order decay process

Assume degradation of waste is proportional to amount of waste remaining in flask

$$\frac{dW}{dt} = -k_1 W$$

We don't measure W, we measure O_2 demand. A reasonable assumption is that O_2 demand is proportional to amount of W.

$\therefore \quad L = k_2 W \qquad L = O_2$ demand remaining

We can now express L as

$$\frac{dL}{dt} = k_2 \frac{dW}{dt} = -k_1 k_2 W = -k_1 L \Rightarrow \frac{dL}{dt} = -k_1 L$$

k_1 is BOD reaction constant.

Solution to the equation is $\int \frac{dL}{L} = -\int k_1 dt \Rightarrow L = L_0 e^{-kt}$

L_0 is called <u>ultimate</u> O_2 demand

L is called O_2 demand remaining at time t.

The amount of O_2 demand used in time t is the BOD_t

$$\therefore \quad BOD_t + L_0 e^{-kt} = L_0$$

More traditionally $BOD_t = L_0(1 - e^{-kt})$, L_0 is usually estimated from BOD_5

<u>Example</u> $P = 0.03$, $DO_0 = 9\,mg/L$, $DO_5 = 3\,mg/L$, $k = 0.22/d$

What is BOD_5? $\quad BOD_5 = \frac{9-3}{0.03} = 200\,mg/L$

What is L_0 $\quad BOD_5 = L_0(1 - e^{-kt}) = L_0(1 - e^{-(0.22)(5)})$

$$L_0 = \frac{200\,mg/L}{(1 - e^{-0.22(5)})} = 299.8\,mg/L$$

What is L_5 $\quad L_5 = L_0 e^{-kt} = 299.8(e^{-0.22(5)}) = 99.8\,mg/L$

The rate constant is usually determined by experiment.

k is temperature dependent. A typical correction is

$$k_T = k_{20}\,\theta^{(T-20)} \qquad \theta \approx 1.047$$

CBOD; NBOD

So far: $\text{organic} + O_2 \longrightarrow CO_2 + H_2O + \text{more cells} + \text{byproducts}$

"carbonaceous O_2 demand" (CBOD)

Nitrogen compounds are also metabolized in presence of O_2

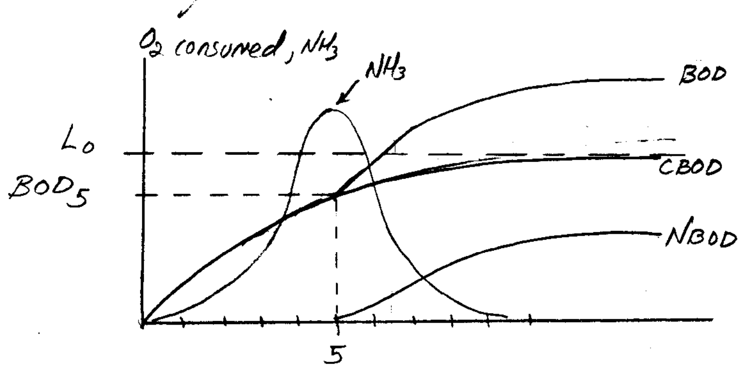
(1) $2NH_3 + 3O_2 \xrightarrow{\text{nitrosomonas}} 2NO_2^- + 2H^+ + 2H_2O$

(2) $2NO_2^- + O_2 \xrightarrow{\text{nitrobacter}} 2NO_3^-$

combination is called "nitrification"

O_2 required to complete the process is called nitrogeneous oxygen demand (NBOD)

Atmospheric N_2 is converted to biologically useful NH_3 & NO_3 by "nitrogen fixation" bacteria & blue-green algae can transform N_2 into NH_3 & NO_3. All other organisms must obtain their nitrogen from these sources.



BOD = CBOD + NBOD

Nitrification takes time, usually more than 5 days. Because of time lag, ammonia is a useful indicator of sewage age & reactor residence time.

Other measures

In addition to CBOD & NBOD

ThOD & COD

ThOD overestimates actual O use because compounds oxidized actually build cell mass and are not mineralized.

Some organic matter is not easily biodegraded – either resistent or toxic.

cellulose, phenol, benzene

COD is a test that chemically oxidizes these materials in about one day – less if dedicated instrumentation is used. COD measures compounds that may not degrade

$\therefore \quad COD \geq BOD_5$

<u>Example</u> Wastewater 30 mg/L N as NH_3. Assume O_2 demand by stoichiometric relations find a) ThOD ($NBOD_u$) b) $NBOD_u/N$ in water

a) $2NH_3 + 3O_2 \rightarrow \cancel{2NO_2^-} + 2H^+ + 2H_2O$

$\cancel{2NO_2^-} + O_2 \rightarrow 2NO_3^-$

overall

$2NH_3 + 4O_2 \rightarrow 2H^+ + 2NO_3^- + 2H_2O$

$* \; NH_3 + 2O_2 \rightarrow H^+ + NO_3^- + H_2O$

Complete oxidization of NH_3 uses 2 mol O_2/mol NH_3

a) $30\,mg/L\text{-}N \cdot \frac{17{,}000\,mg\,NH_3}{14{,}000\,mg\,N} \cdot \frac{1\,mol\,NH_3}{17{,}000\,mg\,NH_3} \cdot \frac{2\,mol\,O_2}{1\,mol\,NH_3} \cdot \frac{32\,000\,mg\,O_2}{1\,mol\,O_2} = 137\,mg/L\text{-}O_2$

b) $NBOD_u = 137\,mg/L - O_2 \qquad N = 30\,mg/L$

$\therefore \frac{NBOD_u}{N} = \frac{137}{30} = \frac{4.57\,mg\,O_2}{mg\,N}$

Total concentration of organic & ammonia N is known as total Kjeldahl nitrogen, TKN. TKN is typically measured.

$NBOD_u \approx 4.57 * TKN$