CIVE 3331 - ENVIRONMENTAL ENGINEERING
Spring 2003

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Water Properties

Water is one of three environmental media of great importance to people. We can survive a few minutes with out air, a few days without water, a few weeks without food – these three "necessities" have parallels in environmental engineering; air, water, soil. We will start with water because historically that has been the emphasis, it is a substance we are famiar with, and it is the media that has received the most attention until recently.

Water quality affects water use; water use affects water quality – this statement integrates civilization's relationship with water.

Water has multiple uses:

1. Drinking (physiological), bathing (hygene), swimming (recreation).

2. Agricultural (consumptive use) to grow food and products.
3. Industrial (product water and process water).
4. Energy production (heat transfer medium and hydropower).
5. Ecological (maintain desirable ecosystem properties).

Each intended use has a different quality requirement, and each use diminishes the water quality in some fashion. Consider some examples.

Water as a heat transfer medium. Main property of interest is the high enthalpy of vaporization (~2000 kJ/kg). Color, taste, odor are relatively unimportant. Mineral content and pH are of some importance.

Water in agriculture. Main properties are water's ability to participate in the construction of cell mass during photosynthesis and as a transport medium for nutrients and minerals. Mineral content is critical (as certain ions can damage cells because of adverse osmotic pressures). Water is also a building block of carbohydrates used in cell mass construction and energy production.

Water in industrial processes. Properties of interest are heat transfer and polar solvency. Water can ionize many residues and remove them from the final product. Water is often a medium in which other important reactions are conducted. Steam (high P and T) is used as a energy source and retort fluid for important processes (steam reforming of hydrocarbons is a good example).

Water Properties

Water is a polar molecule (at microscopic level it exhibits a positive side and negative side). This dipole moment helps explain some interesting physical and thermodynamic properties.

Water density decreases with temperature near the liquid-solid phase change – ice floats. Attributed to the crystal structure requiring specific spacing between these "polar" molecules.

Liquid stratifies according to temperature – warm water floats; thus thermal stratification is possible. Plays a role in lakes during winter.

Water has a high melting point and boiling point for its molecular weight.

Water H_2O	=	18g/mol.
Methane CH_4	=	16 g/mol.
Acetaldehyde, oxime C_2H_5NO	=	59g/mol .

At 1 atm 115^oC water is a **gas**, methane is a **gas**, Acetaldehyde, oxime is a **gas**.

At 1 atm, 100^oC water is a **gas/liquid**, methane is a **gas**, Acetaldehyde, oxime is a **liquid**.

At 1 atm, 20^oC water is **liquid**, methane is a **gas**, Acetaldehyde, oxime is a **solid**.

At 1 atm, 0^oC water is a **solid/liquid**, methane is still a **gas**.

At 1 atm,-161^oC water is a **solid**, methane is a **liquid**.

At 1 atm,-182^oC, water is a **solid**, methane is a **solid**.

Water's triple point exists as terrestrial temperatures and pressures. Water has a high enthalpy of vaporization and high specific heat (as a liquid). These "properties" help water absorb energy and moderate temperatures on a global scale.

Universal solvent – polar and non-polar compounds dissolve to some extent in water. It serves as a medium for transport of nutrients and wastes because of this property.

Hydrology and the hydrologic cycle

Hydrology is the study of the occurrence, distribution, movement, and chemistry of water of the earth. Hydrologic forcing processes govern flow and storage. These processes are <u>precipitation</u>, <u>infiltration</u>, <u>runoff</u>, and <u>evaporation</u>. Precipitation is the amount of atmospheric water that falls onto the surface of the earth. Infiltration is the amount of water that seeps into soil and eventually reaches the saturated zone. Runoff is the amount of precipitation that neither infiltrates nor immediately evaporates. Evaporation is the amount of surface water that returns to the atmosphere by volatilization and transpiration.

The hydrologic cycle is the name given to the dynamic process where water is transported from the subsurface to the surface to the atmosphere and back again. The concept of the hydrologic cycle is central to an understanding of the occurrence of water and the development and management of water supplies.

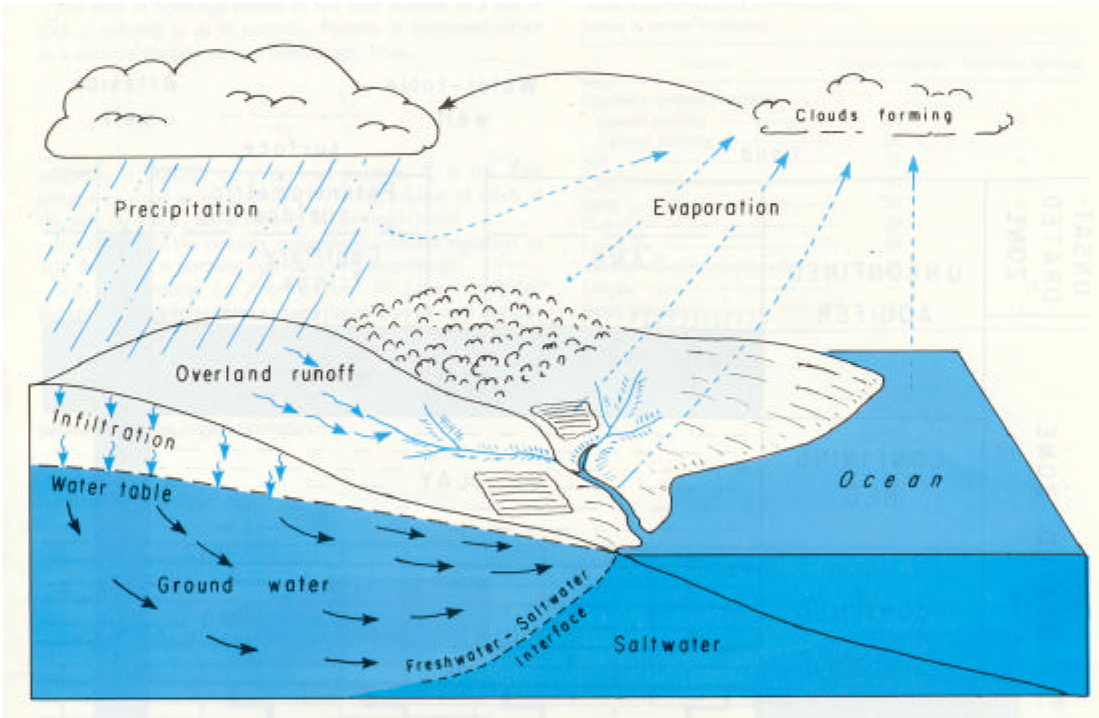


Figure 1. Hydrologic Cycle

(from Heath, R.C., 1983. Basic Ground-Water Hydrology, USGS Water Supply Paper 2220)

Although the hydrologic cycle has neither a beginning nor an end, it is convenient to discuss its principal features by starting with evaporation from vegetation, from exposed moist surfaces including the land surface, and from the ocean. This moisture forms clouds, which return the water to the land surface or oceans in the form of precipitation.

Precipitation occurs in several forms, including rain, snow, and hail, but only rain is considered in this discussion. The first rain wets vegetation and other surfaces and then begins to in- filtrate into the ground. Infiltration rates vary widely, depending on land use, the character and moisture content of the soil, and the intensity and duration of precipitation, from possibly as much as 25 mm/hr in mature forests on sandy soils to a few millimeters per hour in clayey and silty soils to zero in paved areas. When and if the rate of precipitation exceeds the rate of infiltration, overland flow occurs.

The first infiltration replaces soil moisture, and, thereafter, the excess percolates slowly across the intermediate zone to the zone of saturation. Water in the zone of saturation downward and laterally to sites of ground-water discharge such as springs on hillsides or seeps in the bottoms of streams and lakes or beneath the ocean. Water reaching streams, both by overland flow and from ground-water discharge, moves to the sea, where it is again evaporated to perpetuate the cycle. Movement is the key element in the concept of the hydrologic cycle. Some "typical" rates of movement are shown in table 1, along with the distribution of the Earth's water supply.

Table 1. RATE OF MOVEMENT AND DISTRIBUTION OF WATER

Location	Rate of Movement	Water Supply Fraction
Atmosphere	100’s Km/day	0.001
Surface Water	10’s Km/day	0.019
Groundwater	m/day	4.12
Polar regions and glaciers	m/year	1.65
Oceans	------	93.96

[from L`vovich, M.I. 1979. World water resources and their future (English translation edited by R.L. Nace): American Geophysical Union, Washington D.C., 415 p.]

The hydrologic cycle concept can be used to estimate the time water spends in different compartments of the cycle. The typical residence time is important in estimating the effects engineered facilities might have on either the quality or quantity of water in the compartments.

Tables 2 and 3 illustrate the residence times based on water budget calculations. Observe that the exchange rate for groundwater is nearly three orders of magnitude smaller than for surface water and the residence time is consequently nearly three orders of magnitude larger. This exchange rate difference means that polluted groundwater will take far longer to restore than an equivalent volume of surface water by allowing the system to "cycle" naturally. This obvious result is the principal argument for groundwater protection planning that is mandated by the federal and most state regulators.

Table 2. Freshwater exchange rates in different compartments of hydrosphere

Compartment	Volume (Km^3)	Volume (mi^3)	Fraction of supply	Exchange rate (yr)
Ice and glaciers	24,000,000	5,800,000	84.945	8,000
Groundwater	4,000,000	960,000	14.158	280
Reservoirs	155,000	37,000	.549	7
Soil moisture	83,000	20,000	.294	1
Vapor	14,000	3,400	.049	.027
Rivers	1,200	300	0.004	0.031
Total	28,253,200	6,820,700	100.000	

from L`vovich, M.I. 1979. World water resources and their future
(english translation edited by R.L. Nace): American Geophysical Union, Washington D.C., 415 p.

Table 3. Global Water Supply

Compartment	Surface Area (km^2)	Water Volume (km^3)	Supply Fraction	Compartment Residence Time
Oceans	361,000,000	1,230,000,000	97.2 %	1000 years
Atmosphere	510,000,000	12,700	0.001 %	9 days
Rivers		1,200	0.0001%	2 weeks
Groundwater	130,000,000	4,000,000	0.31 %	100 years
Lakes	855,000	123,000	0.009 %	10 years
Ice and Glaciers	28,200,000	28,600,000	2.15 %	10,000 years

(Botkin and Keller, 1998. Environmental Science, J. Wiley & Sons, New York, pp 393-393)

The hydrologic balance is simply the expression of the conservation of mass in hydrologic terms. Generally it is expressed as a rate (or volume) balance as The hydrologic equation is the fundamental tool in groundwater hydrology to describe amounts of water in storage in different compartments at different scales. The equation expressed in "words" is

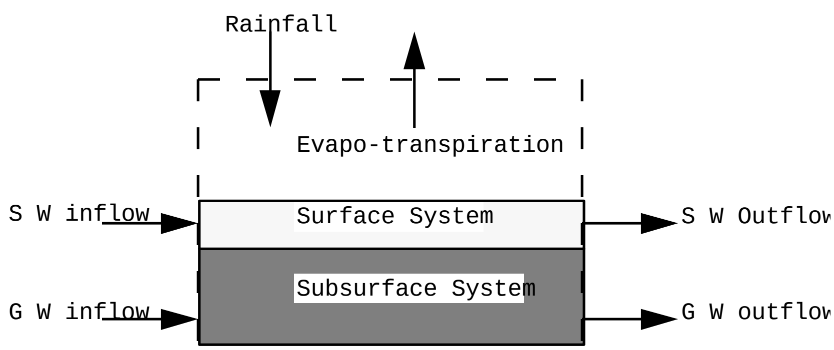
Rate of inflow - Rate of outflow =

Rate of change of storage + Rate of internal mass generation.

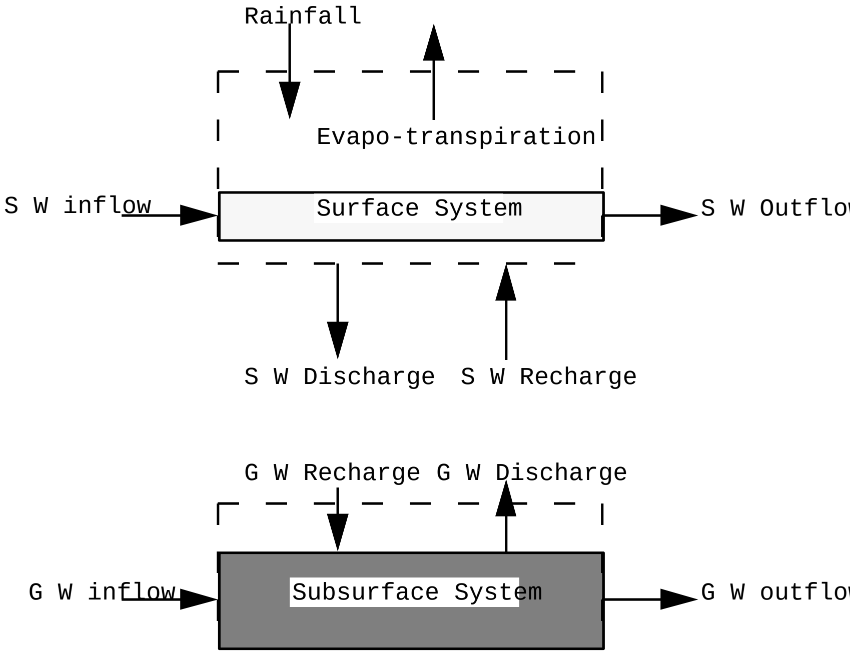
Symbolically, (as a rate equation) it can be represented as:

$$\frac{dI}{dt} - \frac{dO}{dt} = \frac{dS}{dt} + \frac{dG}{dt}$$

Where I is the inflow volume, O is the outflow volume, S is the storage volume, and G is the generated volume. A sketch of the balance could look like:



The two systems, surface and groundwater can be further divided and the hydrologic balance for each system examined:



Thus, the groundwater hydrologic balance would be written as:

Recharge + Inflow - Discharge - Outflow = Storage + Generation

The terms in various sources in the groundwater literature will have different names, but the components of the balance will be obvious from the context. Discharge (in our picture) would also include losses due to plant uptake of water, and direct evaporation in some basins.

Water Budget Analysis

A water budget is a model that balances the inputs, outputs, and storage of water in a system. A water budget is a particular solution to the hydrologic equation for a given basin, region, etc. It is analogous to the material balance methods discussed in the earlier lectures, just the names of the arrows re changed. If we are also tracking pollutants, like before, we will have hydrologic and contaminant balance equations. Below is an example of a water budget diagram for the entire United States of America. The example that follows illustrates how the water budget is created.

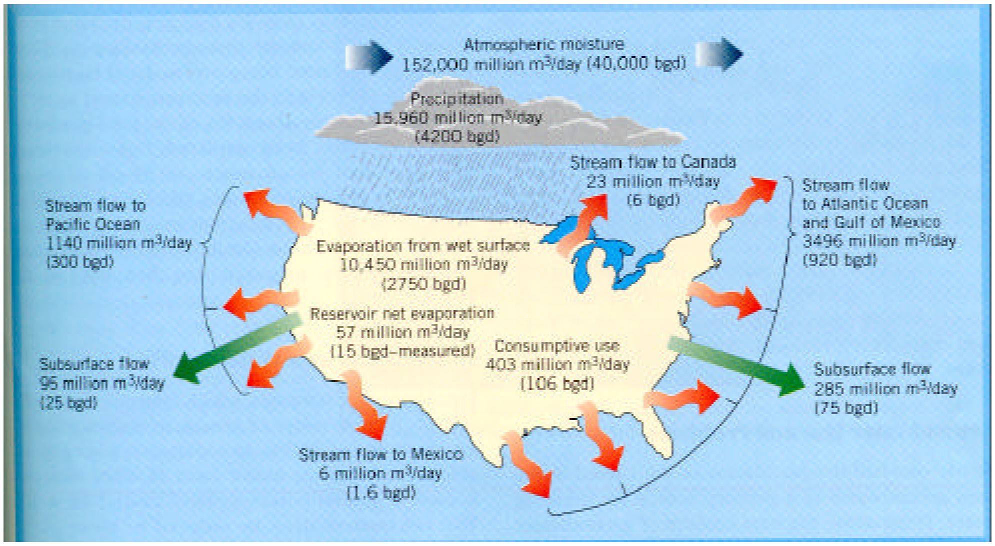


Figure 2. Water Budget for the United States

(from Botkin and Keller, 1998. Envrionmental Science, J. Wiley & Sons, New York)

Example

A ground-water basin in a coastal area has an area of 200 mi^2. The land area is 195 mi^2 and the area of the rivers is 5mi^2. The hydrologic inputs and outputs have the following long-term average annual values: precipitation, 35 in./yr; evaporation, 23 in./yr.;direct runoff, 3 in./yr/; baseflow, 6 in./yr.;streamflow, 9 in./yr.; subsea outflow, 3 in./yr.

Prepare an annual water budget for the whole basin, the streams, and the groundwater system.

1) Sketch the system.
2) State governing principles
3) Identify inflows, outflows, storages, etc.
4) Insert numerical values
5) Interpret results

Annual Water Budget								
Inputs	(in/yr)	(cu.ft./yr)	Outputs	(in./yr.)	(cu.ft./yr)			

Nearly all exploitable water exists in the hydrologic cycle. (See table 5.1 of textbook)

96% oceanic. (not easily used)

2% ice and glaciers (not conviently located)

1.09% groundwater (about ½ of this water is unusable)

0.01 % fresh surface water

Total proven water reserves (globally):

23.5×10^{15} m^3 (9 grams of water ~ 23×10^{15} molecules!)

USA usage:

403 million cubic meters a day

0.0000017 % of world's reserves in use in the USA on any given day.

Only a small fraction of the reserves are available for economic use. The concept of consumptive use means that the water is used an such a fashion that it is unavailable for near-future use or is removed from the portion of the hydrologic cycle where renewal is on a short (years) time frame.

Engineering challenges and concerns are: water supply, flood protection, waste discharge; ecological (quantity and quality protection); disease control.

Pollutants

These are materials that render the water unfit for intended use. Pollutants can be put into several categories:

Pathogens – disease causing materials such as: Bacteria, protozoa, parasites, fungi, virus, prions(maybe)

Diseases related to water are further classified by how they infect the people.

Waterborne- carried by water; cholera

Water based – schistosomiasis (from contact)

Water related - malaria

Watershed - lack of water; hygene.

Fecal coliform is used as an indicator of pathogen potential. High FC = High probability of pathogens in a water.

Oxygen demanding wastes – DO is important indicator of ecological water quality. It affects speciation of chemicals and biochemistry. Fish and other organisms need oxygen to live; otherwise only anaerobic organisms will survive. Important equilibria depend on oxygen in water.

O2 demanding wastes are materials whose presence and natural degradation uses O2 and reduces DO in water. DO is a measure of the dissolved O2 in water. BOD,COD are measures that indicate the oxygen demand of a water sample.

Nutrients

Nutrients are materials essential for life. Pollutants because they stimulate growth and exceed the carrying capacity of the particular ecosystem. Nitrogen (N) and Phosphorous (P; PO_4) are usually the limiting nutrients in natural systems. Most wastewater control is focused on control of these materials. Nutrient enrichment accelerates a process called eutrophication. N compounds (NO3) are tixic to infants. P is usually quite scarce in natural systems – modern civilization has greatly changed P (increased) in the ecosystem.

Salts

Significant impact on agriculture. High concentrations make water unsafe to drink – cause cells to lose water (osmosis). RO can remove salts, but are energy intensive. Trace amounts of salts (minerals) are required for life.

Thermal pollution

Saturation DO decreases as temperature increases. Aquatic diversity decreases as temperature increases. Certain dissolved materials precipitate at elevated temperatures (boiler scale).

Metals

Most metals are toxic – toxicity varies depending on redox state. Some are essential trace nutrients, but toxic in large amounts. DO and pH play big role in metal availability. Usually low DO and low pH are problems with metals.

Pesticides and VOC

Organophosphates (pesticides) and carbamates are endocrine disruptors and cholinesterase (nerve-agent) inhibitors. Impact reproduction, immune system, and CNS. In large does they are lethal to humans. Chlorinated hydrocarbons (herbicides) are carcinogens and endocrine disruptors. VOCs are used as solvents and fuels. Carcinogens and mutagens. Extremely common in groundwater. Some are toxic at low doses.

Dissolved Oxygen and Oxygen Demand

Surface water systems are used for:

Drinking water; agriculture, aquatic habitat, contact recreation, and waste disposal.

Three distinct uses/needs:

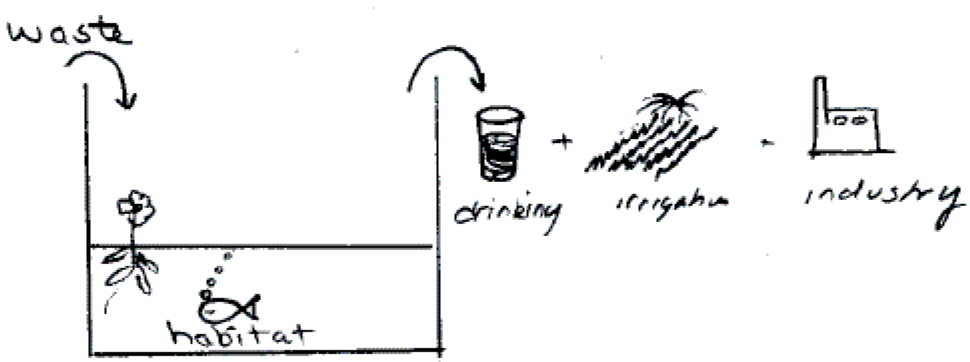


Figure 3. Distinct Water Needs

Aquatic life needs a certain level of DO to survive. Wastes are metabolized by microorganisms – this metabolism uses O2.

Aerobic consumption:

Organic + $\mathbf{O_2}$ + microorganisms

=> CO_2 + H_2O + more microorganisms + by products (NO_3,PO_4,SO_4,…)

Anaerobic consumption:

Organic + ___ + microorganisms

=> CO_2 + H_2O + more microorganisms + by products (NH_3,H_2S,CH_4,…)

The amount of O2 required in the first path to oxidize all the waste is called the biochemical oxygen demand (BOD). It is comprised of two parts; the CBOD (Carbonaceous) and NBOD (Nitrogeneous).

5-day BOD Test

Ideally one would measure all the O2 required to oxidize waste, but it usually takes too long. In practice only part of the time required is actually used, the interval by convention is 5-days. Figure 4 is a sketch that illustrates how the test is run. A sample of water is placed into a bottle and the dissolved O2 is measured. Then the bottle is sealed for five days. Then the bottle is opened and the DO is again measures. Assuming there is some O2 remaining, a mass balance on the O2 in the bottle determines the BOD (or the amount of O2 used up) during the interval.

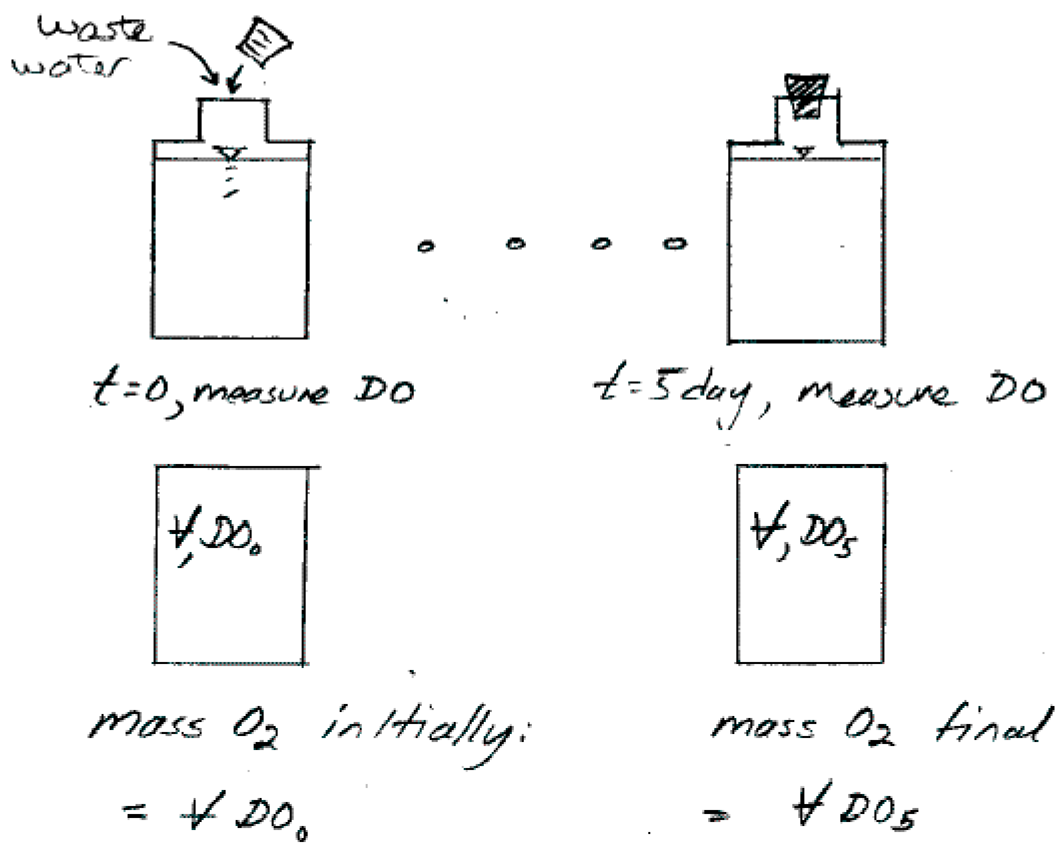


Figure 4. 5-Day BOD sketch

The mass balance equations are:

Δ O2 Mass = Mass Initial – Mass Final = $V*DO_0 - VDO_5$

BOD with Dilution

Usually the waste has a very high BOD so only a fraction of the waste is added and the remainder is clean water. In this case the sketch and computations are:

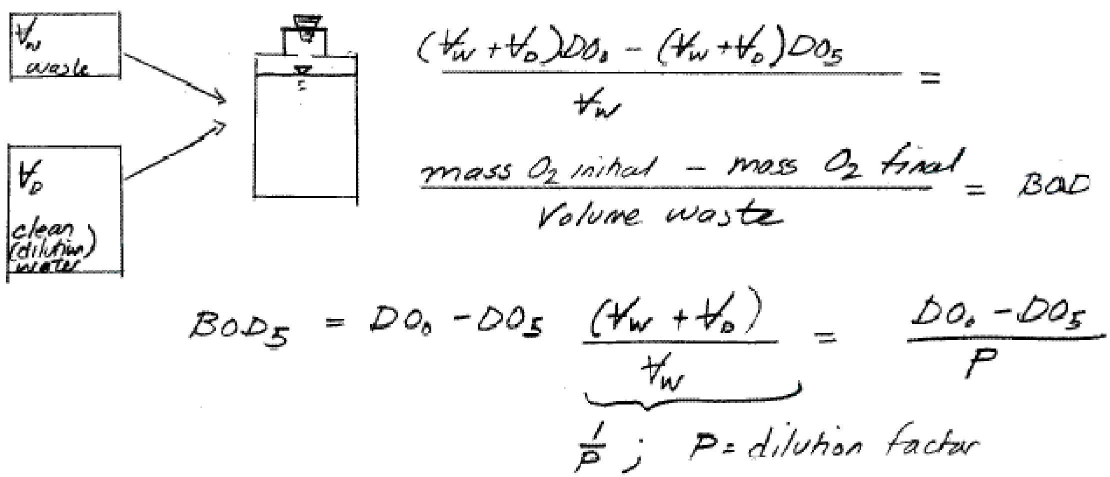


Figure 5. BOD with dilution water

Standard BOD bottles are 300mL, so the value P is usually P = V_{waste}/300mL.

Important concepts:

BOD is a measurement that indicates relative oxygen demand of a waste water. BOD is reported in concentration units. BOD is not itself a chemical, compound or organism – it is an observed response to the presence of materials that are degraded by organisms.

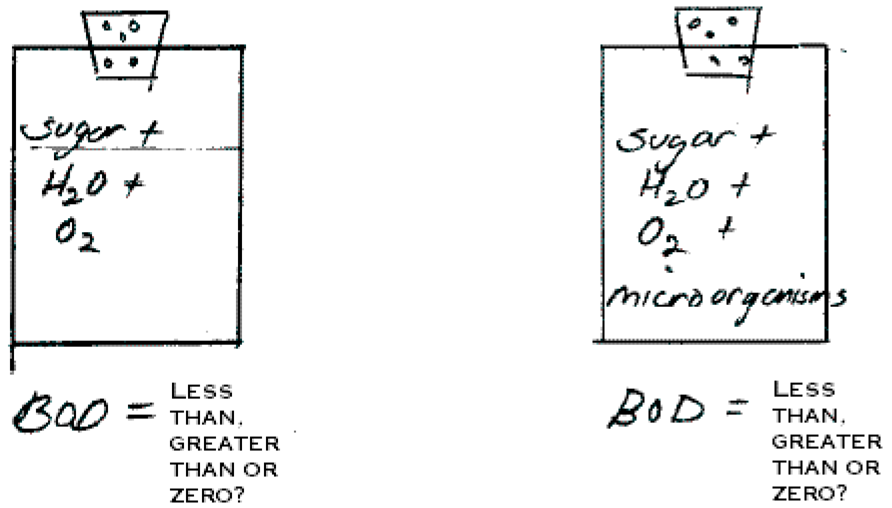


Figure 6. BOD concepts - which has non-zero BOD?

Example:

10mL sewage + 290 mL water. DO_0 = 9 mg/L. Desire at least 2 mg/L drop in DO, and mimimum DO > 2.0. For what range of BOD_5 is this dilution useful?

Sketch –

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

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

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

From these calculations we conclude that for this dilution will be useful for BOD_5 ranging from 60 to 210 mg/L. In this experimental design, we would use a different dilution if the DO limits are exceeded.

The dilution water itself exherts its own BOD, so a blank test is conducted to determine the contribution to BOD form the sewage and the diluent water.

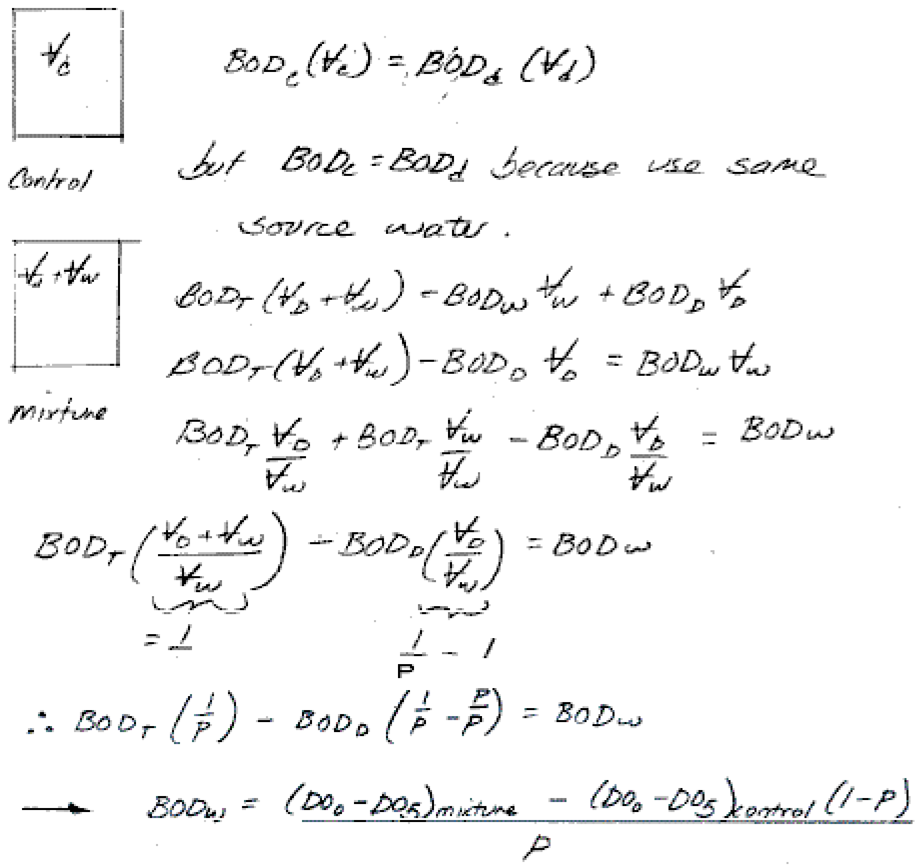


Figure 7. BOD with diluent that exherts its own BOD

BOD as a 1st-order decay process

Assume that the degradation of waste is proportional to the amount of waste remaining

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

But we don’t measure W we measure O2 demand, which we assume is proportional to W.

Therefore we have $L = k_2 W$, where L is the O2 demand remaining (unused). We can now express L in terms of the constants of proportionality as $\frac{dL}{dt} = k_2 \frac{dW}{dt} = -k_1 k_2 W = -k_1 L$. The constant k_1 is called the BOD reaction constant or the BOD decay constant.

The solution to the differential equation is obtained from:

$$\frac{dL}{dt} = -k_1 L;\ \text{first separate the variables}$$
$$\frac{dL}{L} = -k_1 dt;\ \text{then integrate both sides; } \int \frac{dL}{L} = -k_1 \int dt$$
$$\ln(L) = -k_1 t + c \ \text{ or } \ L = L_0 e^{(-k_1 t)}$$

The L_o value is called the ultimate oxygen demand. L is the oxygen demand remaining (unused). The amount of oxygen demand used up in a given interval of time is called the BOD_t

Thus

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

More conventionally it is expressed as

$$BOD_t \quad = \quad L_o (1-e^{-kt})$$

The ultimate demand is usually estimated from the 5-day BOD value; the rate constant is usually determined by experiment. This constant is highly temperature dependent. A typical correction formula is $k_T = k_{20}(1.047)^{(T-20)}$, where T is temperature in degrees Celsius.

CBOD and NBOD

So far we have talked about a portion of aerobic consumption:

Organic + $\mathbf{O_2}$ + microorganisms

=> CO_2 + H_2O + more microorganisms + by products (NO_3,PO_4,SO_4,…).

This portion is called the carbonaceous oxygen demand (CBOD). Nitrigen compounds are also meatabolzed in the presence of oxygen.

(1) $2NH_3 + 3O_2$ + nitrosomas => $2NO_2^- + 2H^+ + 2H_20$

(2) $2NO_2^- + O_2$ + nitrobacter => $2NO_3^-$

This process (both equations) is called nitrification. The O2 required in nitrification is called the nitrogeneous oxygen demand (NBOD). Atmospheric N2 is converted to biologically useful NH3 and NO3 by “nitrogen fixation.” Bacteria, blue-green algae, and some legumes (in symbosis with nitrogen fixing bacteria) can obtain nitrogen compounds directly from the atmosphere. All other organisms must obtain their nitrogen from these sources.

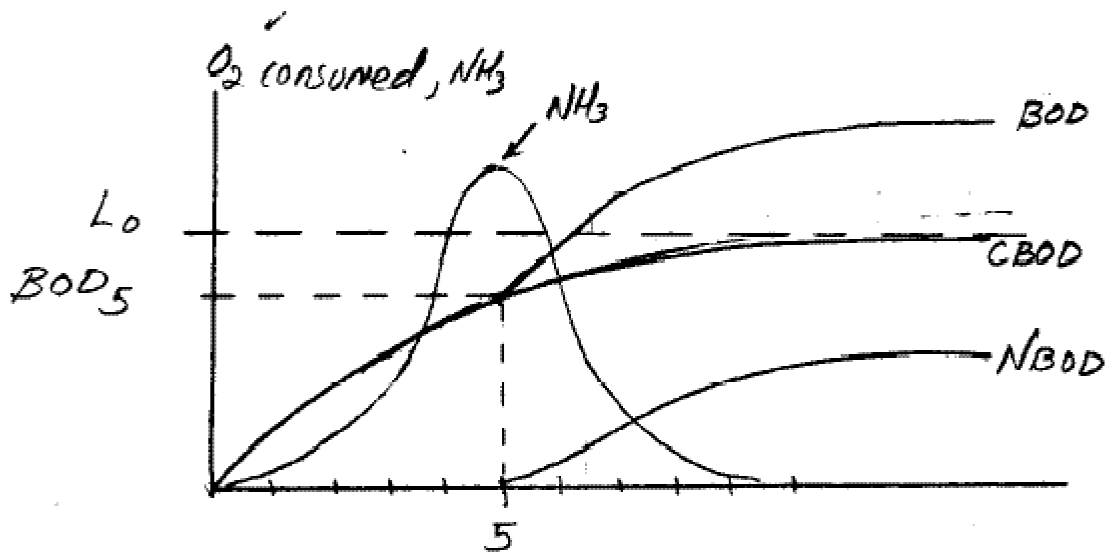


Figure 8. CBOD,NBOD versus time

Nitrification takes some time as suggested in Figure 8. Because of the time lag, ammonia is a useful indicator of sewage age and reactor residence time – it is not terribly useful for desing, but it is extremely useful for diagnosing upsets and reactor flow restrictions that are not apparent at first glance. Figure 9 is a photo of a typical treatment plant with parallel reactors. Ideally the residence time of each reactor is supposed to be about the same (meaning the flow is supposed to be the same). If there is a big discrepance in ammonia at the end of each reactor, that is an indication of nonuniform flow – and the engineer and operator need to figure out why, and if it is a problem.

Figure 9. Typical Wastewater Reactor (s) with Parallel Reactors

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