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INTRODUCTION TO WATER POLLUTION

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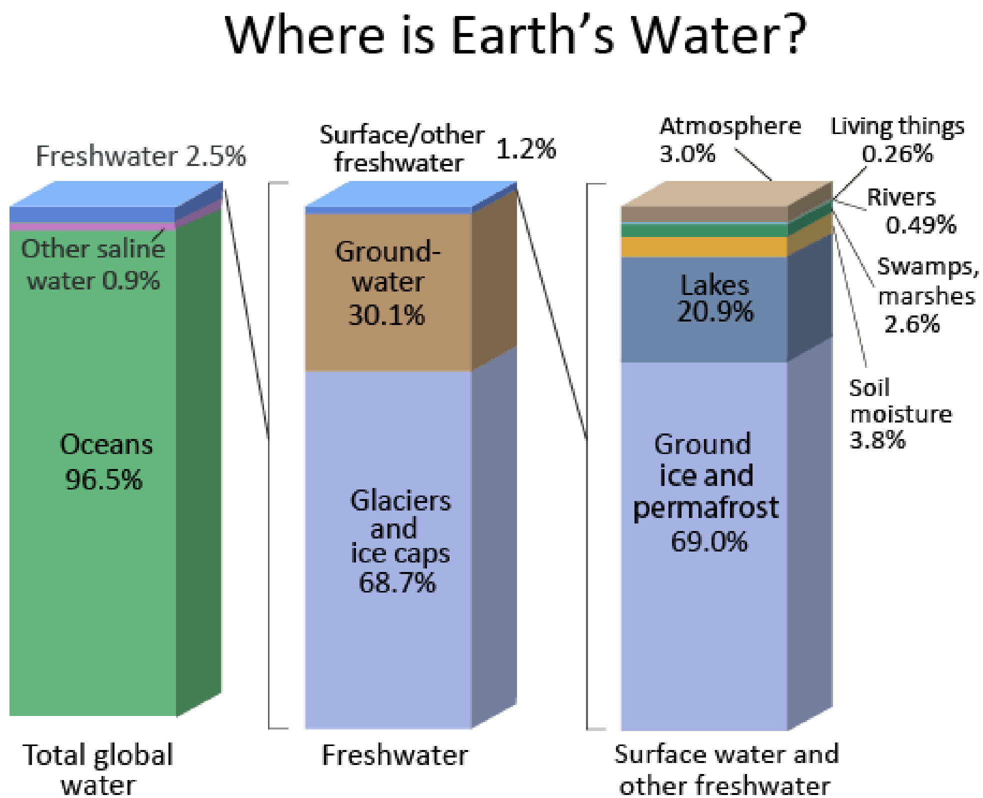
WATER AVAILABILITY

The majority of water on Earth is saline with 99.9% of this found in seas and oceans.

Saline water **97.5%**

Fresh water **2.5%**



Earth's water availability

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FRESH WATER AVAILABILITY

Most of this fresh water (2.5%) is locked up as ice caps and glaciers.

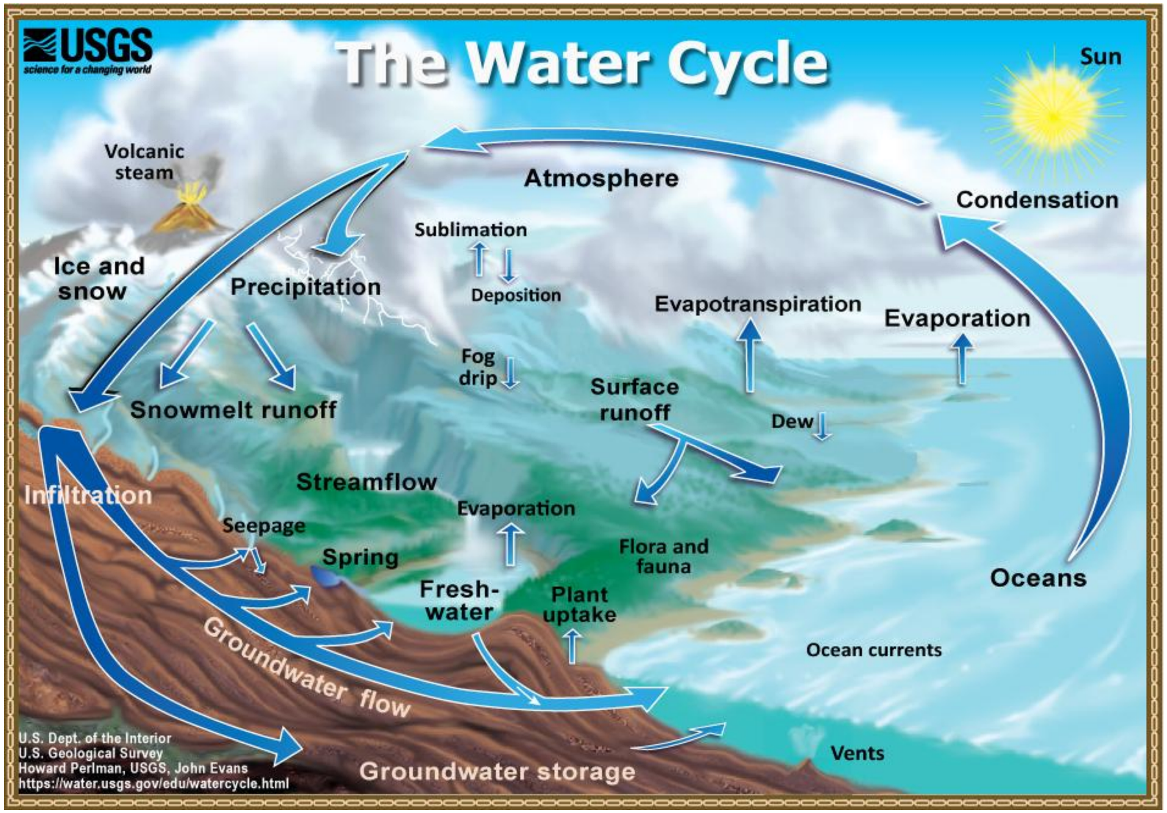
Polar ice caps and glaciers 77.2%

Liquid and vapor 22.80%

- 22.40% Groundwater, aquifers and soil moisture
- 0.35% Lakes
- 0.01% Rivers
- 0.04% Atmosphere

So, while there appear to be lots of water about, **there is in reality very little which is readily available for use by humans.**

The **hydrologic cycle** or **water cycle** describes the continuous movement of water on, above and below the earth's surface.



Water cycle

By Howard Perlman from USGS licensed under Public Domain

HYDROLOGICAL CYCLE

Since the cycle is continuous, there is no actual beginning or end, so we can begin anywhere.

There are four basic processes that make up this cycle:

- Precipitation (*P*)
- Evapotranspiration (*ET*)
- Infiltration (*I*)
- Runoff (*R*)

The hydrological cycle can be represented as: $P = ET + I + R$

This is the **water balance**.

Natural water is **never pure** (H_2O). It always contains **impurities** such as clay, silts, pollen, microorganisms, …

Sources of impurities

- soil-weathering
- biological activities
- …

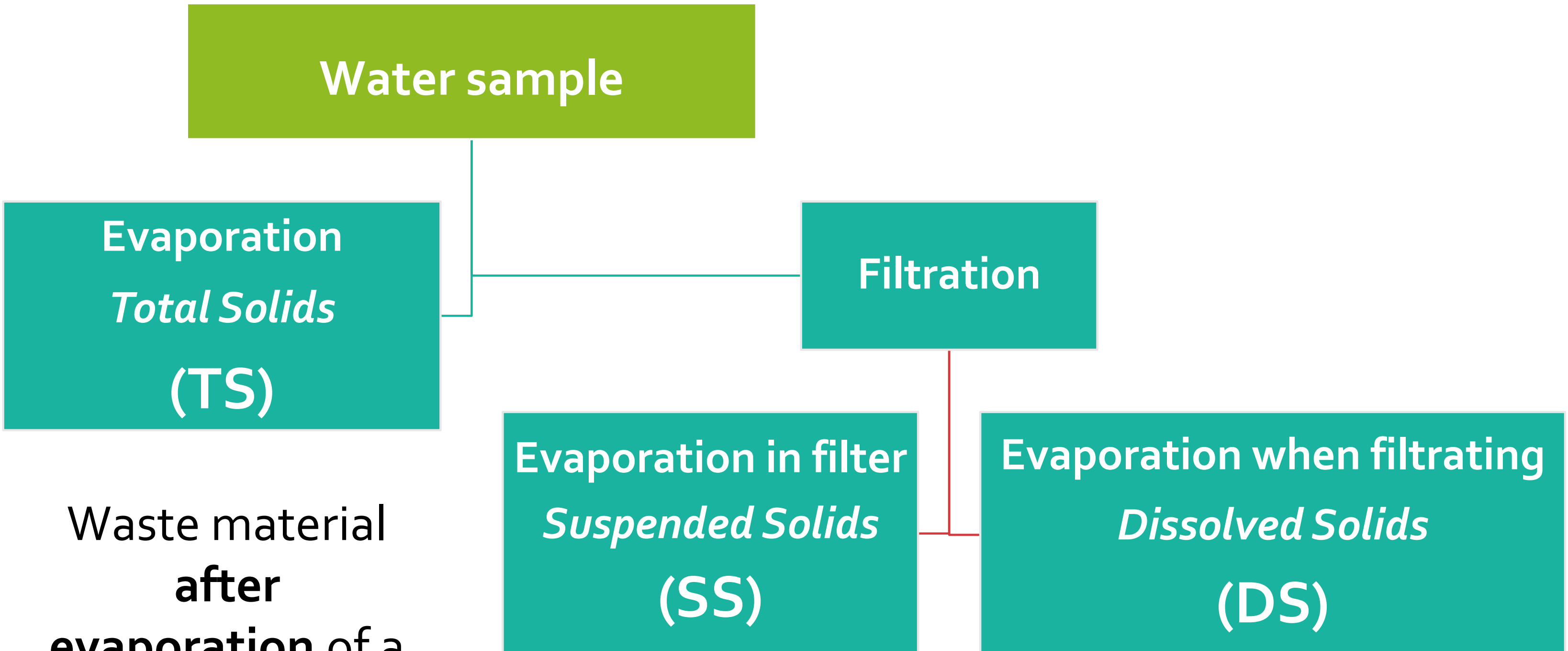
Water impurities

Image by Martin Str from Pixabay licensed under CC0

Impurities can be classified as follows:

- **Dissolved constituents**. Include ions and organic compounds. Determine the chemical properties
- **Suspended constituents** or **particulate constituents**. Include clays and other silicates, colloids and microorganisms.

DETERMINATION OF IMPURITIES



Waste material **after evaporation** of a sample and its subsequent drying in an oven (105ºC)

Portion of total solids **retained** by a filter

Portion that **passes** through the filter

1.1. WATER POLLUTANTS AND SOURCES

Apart from natural impurities, water may contain other compounds introduced by **anthropogenic effluents** that may make it unsuitable for different uses.

Water pollution is the direct and indirect introduction, as a result of human activity, of materials or energy into the water which may be harmful to the quality of aquatic ecosystems, or which impair or interfere with the uses of this resource.

Anthropogenic sources include direct discharge of sewage, storm-water and runoff from agricultural and industrial lands.

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The concentrations above which water impurities and pollutants adversely affect a particular water use may differ widely.

Water quality requirements, expressed as **water quality standards,** are **use-specific**:

- Drinking-water supply
- Industrial processes
- Irrigation
- Recreation
- …

Tap Water

Black faucet by Karolina Grabowska from Pixabay licensed under CC0

Effects of the pollutants

1. <u>Addition of oxygen demanding materials</u>

These materials include food waste, dead plant/animal tissues, and other biodegradable organics.

Inputs of readily oxidizable materials cause Dissolved Oxygen (**DO**) concentration to fall downstream. The degree of oxygen consumption by biologically-mediated oxidation of these materials is called Biochemical Oxygen Demand (**BOD**).

Sources: sewage and industrial wastes from food-processing plants and paper mills.

Effect: **Deoxygenation**

2. Addition of nutrients

Both nitrogen and phosphorous, along with carbon, are essential nutrients for growth. But too much N and P in the water causes algae to grow faster than ecosystems can handle and, it becomes polluted.

Sources: runoff from agriculture, sewage (detergents) and effluents from food-processing plants.

Effects: **Eutrophication** and a fall in dissolved oxygen.

Eutrophication

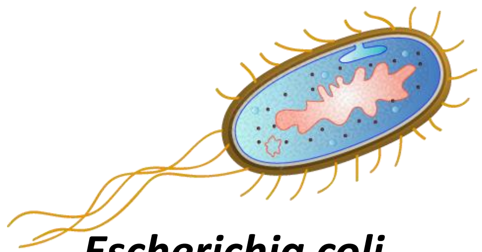
by RM Visuals from Flickr licensed under CC BY 2.0

3. Addition of pathogens

A pathogen is any agent that causes disease in animals or plants. Testing water for each of the disease causing agents is difficult and expensive, therefore, coliform levels are measured.

Sources: sewage discharges or defecation in water bodies.

Effects: **Transmission** of **diseases** (cholera, typhoid, yellow fever, salmonellosis, and shigellosis).



Escherichia coli

by Database Center for Life Science (DBCLS) from Wikimedia licensed under CC BY 3.0

Escherichia coli

"E. coli on XLD" by VeeDunn from Flickr licensed under CC BY 2.0

4. Addition of Suspended Solids

Suspended Solids (SS) are particles too large to dissolve quickly and too small to settle out of suspension.

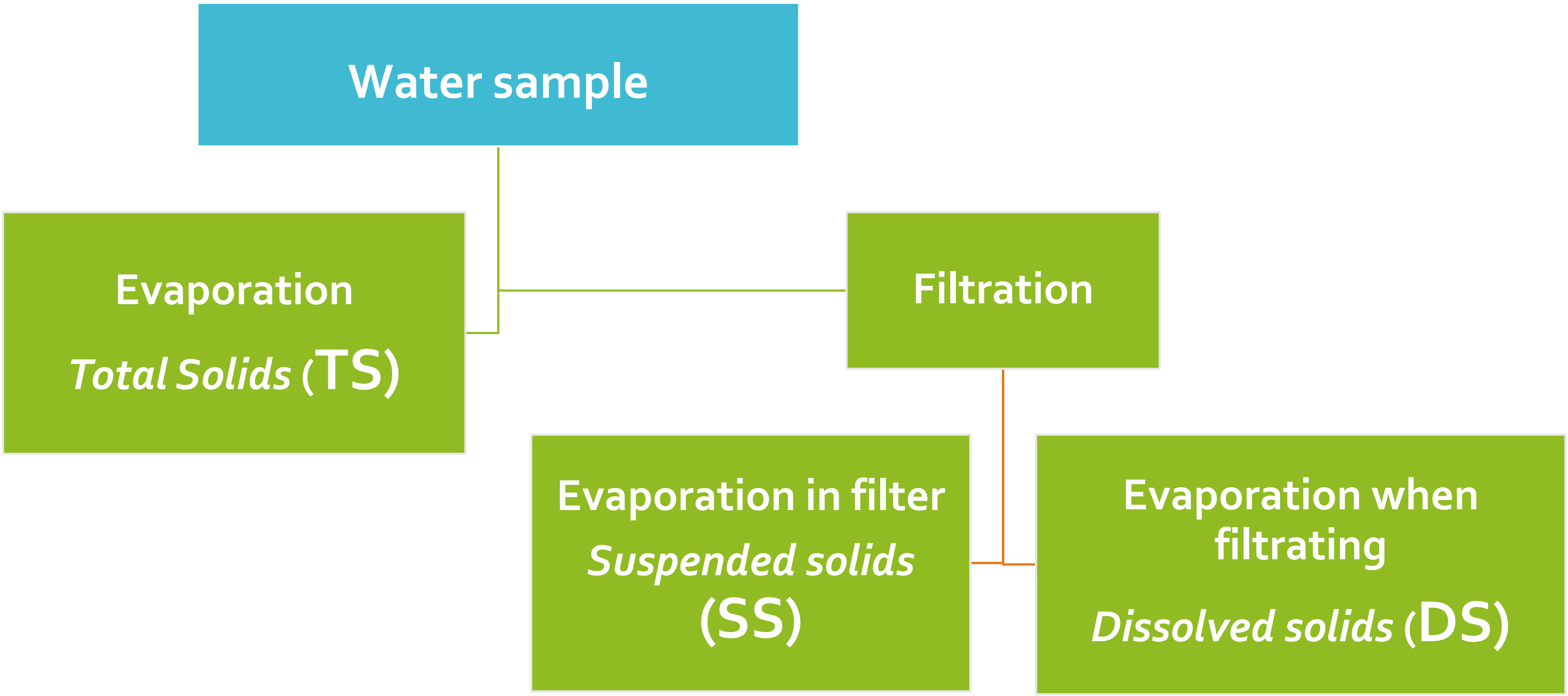
They consist of silt, clay, fine particles of inorganic and organic matter, soluble organic compounds and microorganisms.

Sources: natural (soil weathering, runoff, biological activity,...) and anthropogenic sources (industrial and agricultural discharges)

Effects: **Turbidity**

Different water turbidities in eastern San Salvador Island, Bahamas

CHEMICAL COMPOSITION OF PARTICLES



SS and **DS** can be further subdivided:

- **Volatile Solids** (**VS**): solids that are volatilized and burned off when *SS* or *DS* are ignited (550 ºC). ***VS* ≈ Organic Matter**
- **Fixed Solids** (**FS**): waste material after *SS* or *DS* are ignited

5. Addition of salts

Fresh water contains alkaline salts (NaCl), calcium and magnesium salts and organic salts in natural way. But this natural salinity may be increased by human activities. They add ammonia salts, chlorides and sodium sulfates.

Sources: runoff from agricultural lands, sewage and industrial effluents.

Effects: **Increased salinity and toxicity**.

Salt-affected irrigation field

"Aerial view of fields in central California" by Scott Bauer from Wikimedia licensed under Public Domain

6. Addition of metals and toxic substances

- Zinc, iron, chromium, cadmium, mercury, nickel
- Pesticides

Sources: discharges from residential dwellings, groundwater infiltration, industrial and agricultural discharges.

Effects: **Toxicity**. **Poisoning**.

Water from mine sites draining into the river

"IFWF3 media field trip - acid mine drainage" by Challenge Program on Water and Food from Flickr licensed under CC BY-NC-SA 2.0

7. Thermal pollution

It consists on heating surface waters above natural background temperatures.

Sources: energy/power production and manufacturing plants.

Effects: Loss of temperature-sensitive species, an increase in BOD and decrease in DO

River next to a nuclear plant

"Cooling Tower Power Plant Energy Nuclear Power Plant" from Max Pixel licensed under Public Domain

1.2. WATER QUALITY ASSESSMENT

Water is characterized in terms of:

Physical characteristics

- Total solids
- Turbidity
- Color
- Taste
- Odors
- Temperature

Chemical characteristics

- pH
- [ions]
- Alkalinity
- Acidity
- Hardness
- Conductivity

Biological characteristics

- Number of coliforms
- organisms
- Viruses

PHYSICAL CHARACTERISTICS

1. **Total solids** (TS)
2. **Turbidity.** It is the reduction in clarity of water caused by scattering of visible light by suspended small particles and colloids.

Nephelometry

Comparison of the intensity of the light scattered by a water sample to the light scattered by a reference suspension under the same conditions.

Water turbidity

3. **Color.** It is the reduction in clarity of water caused by the absorption of visible light by dissolved substances and suspended small particles and colloids.

True color (DS)

Apparent color (DS+ SS)

4. **Taste and odors.**

In surface water are caused by a variety of organic compounds from natural and anthropogenic sources.

In groundwater taste and odors are mainly natural in origin; due to organisms action or dissolution of minerals while it percolates.

Brown Muddy Water

The Paraná River by NASA Johnson from USGS licensed under Public Domain

5. **Temperature.** It affects many parameters that impact engineering designs, aquatic life and suitability of water for different uses:

- **Solubility of gases**

Henry's law

$$C_{gas} = k_H \cdot P_{gas}$$

C_{gas} = Solubility of a gas at a fixed temperature

k_H = Henry's law constant

P_{gas} = Partial pressure of the gas

- **Solubility of salts**
- **Rate of biological activity**

CHEMICAL CHARACTERISTICS

1. **pH.** It describes the acid-base properties of a solution.

$$pH = -\log[H^+]$$

It directly influences dosages of chemicals added to reduce hardness and coagulate particles, chlorine disinfection and corrosion control.

2. **Ions.** Cations: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Fe^{2+}, Mn^{2+}

   Anions: HCO^{3-}, SO_4^{2-}, Cl^{-}, F^{-}, NO^{3-}

3. **Alkalinity**. It is the ability of the water to resist changes in pH caused by the addition of acids. This is known as **buffering capacity.** This capacity is favored by carbonates and bicarbonates (CO_3^{2-}, HCO_3^{-}) and hydroxyl ions (OH-).

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4. **Acidity.** It is caused by dissolved CO_2.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

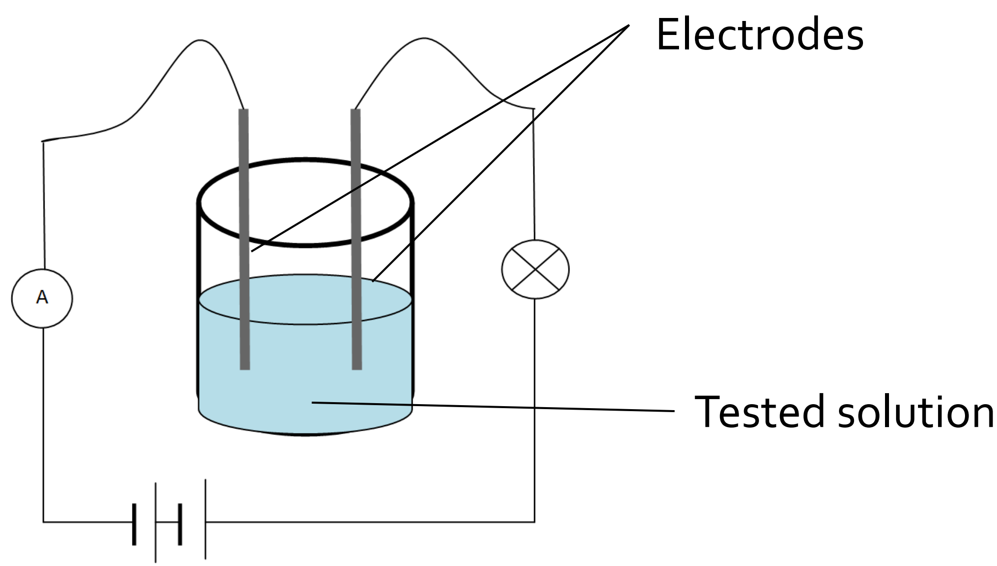
$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

These reactions are reversible and control the pH of water. CO_2 also tends to cause corrosion and consumes reactants in hardness removal processes.

5. **Hardness**. Due to multivalent metallic ions, particularly Ca^{2+} and Mg^{2+}. They are easily precipitated and form a difficult-to-remove scum. Thus, hardness is an important parameter to industry as an indicator of potential precipitation (*e.g.* cooling towers)· It is expressed as mg $CaCO_3 \cdot L^{-1}$.

6. Electrical conductivity (EC). It is the ability to conduct electrical charge. EC is estimated by applying an alternating electrical current to two electrodes in a probe immersed in the sample water and measuring the resulting voltage.

It is related to the concentration of Dissolved Solids (DS ↑ EC↑) and it is expressed as $\mu s \cdot cm^{-1}$ or $\mu\Omega \cdot cm^{-1}$



Electrical conductivity meter

by E. De la Torre

BIOLOGICAL CHARACTERISTICS

All natural waters contain microorganisms. Surface waters contain substantially higher concentrations of bacteria, protozoa, fungi, algae, and viruses. Because it goes through a natural filtration process, groundwater usually has many fewer microorganisms.

Pathogenic organisms found in wastewater may be excreted by human beings and animals who are infected with disease or who are carriers of it.

Pathogenic bacterium in wastewater →

Bacteria	Typhoid fever
	Cholera
	Bacterial dysentery
	Enteritis
Viruses	Infectious hepatitis (Type B)
Parasitic protozoa	Amoebic dysentery
	Giardiasis
	Cryptosporidium
Parasitic worms	Schistosomiasis

Because of the number of pathogenic organism are usually difficult to isolate and identify, microorganisms, which are more numerous and more easily tested for, are commonly used as surrogate organisms (**indicators**) for the target pathogen.

Escherichia coli, an organism found in feces of warm-blooded animals, has historically been the target organism tested for with the **Total Coliform Test**.

Concentrations of total coliform bacteria are reported as the **Most Probable Number** (MPN) per 100 mL.

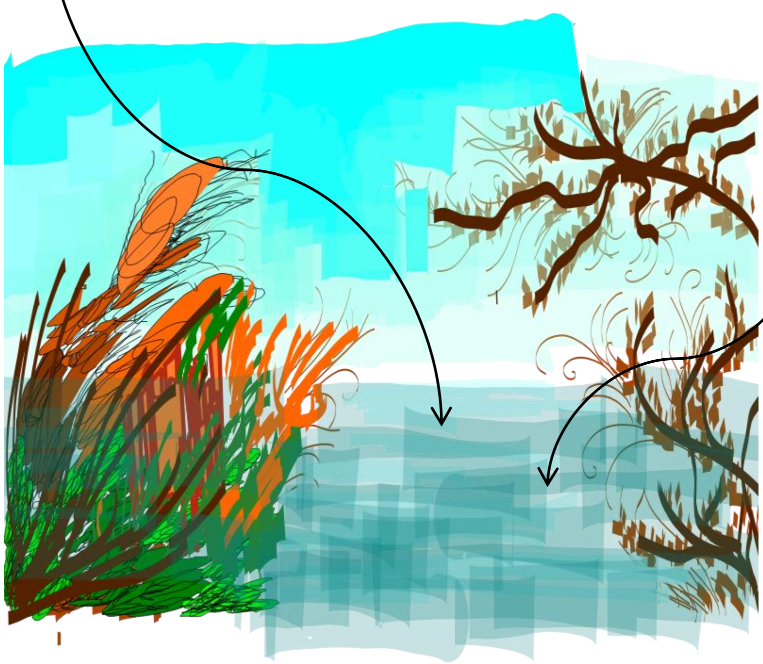
1.3. EFFECTS OF OXYGEN DEMANDING WASTEWATERS

Input of oxidizable organic matter

↓ [DO]

Transfer of O_2 from the atmosphere

↑ [DO]



Waterside

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PARAMETERS THAT RELATE O_2 DEMAND AND ORGANIC MATTER CONTENT

- **Theoretical Oxygen Demand (ThOD)**
- **Total Organic Carbon (TOC)**
- **Chemical Oxygen Demand (COD)**
- **Biochemical Oxygen Demand (BOD)**

Theoretical Oxygen Demand (ThOD) is determined by the chemical formula of the organic matter.

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Total Organic Carbon (TOC) measures the total organic carbon in the water sample. It utilizes heat and oxygen, UV radiation, chemical oxidants, or a combination of these methods to convert organic carbon to CO_2 which is measured with an analyzer.

Compound (1M)	TOC ($g\ C\cdot L^{-1}$)	COD ($g\ O_2\cdot L^{-1}$)
Methane (CH_4)	12	64
Methanol (CH_3OH)	12	48
Formaldehyde (HCOH)	12	32
Formic acid (HCOOH)	12	16

TOC is independent of the oxidation state of the organic matter

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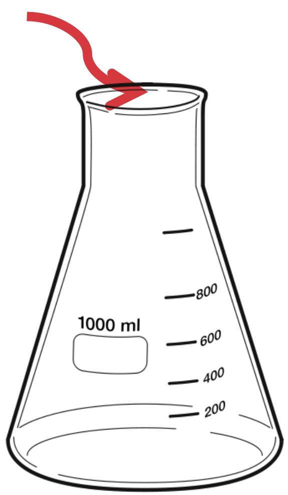
Chemical Oxygen Demand (COD) test measures the organic content of biodegradable and non biodegradable compounds by oxidizing them using a strong oxidizing agent under acidic conditions

Addition of potassium dichromate $K_2Cr_2O_7$



1000 ml Erlenmeyer flask by Xavax and Andrew c. Picture taken from Wikimedia licensed under Public Domain

Reduction of $Cr_2O_7^{2-}$ by Oxidizable compounds

O_2 demand is determined by measuring the amount of oxidant consumed

Heated for 2 h

The **BOD test** measures the amount of oxygen used by microorganisms in the aerobic oxidation of the organic matter over a set period under strictly controlled conditions at 20ºC in dark.

This test is based on the premise that all **biodegradable** organic matter contained in a water sample is oxidized to CO_2 and H_2O by microorganisms using O_2. For example, the oxidation of glucose:

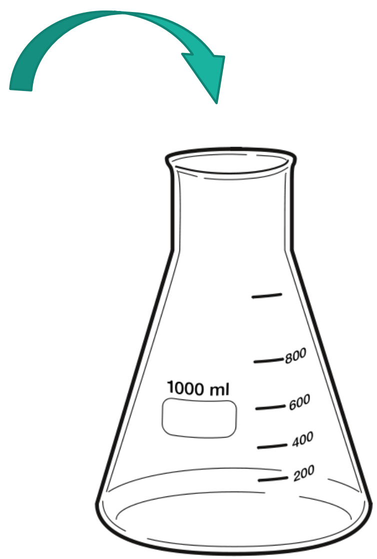
$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

↑ BOD ↓ Quality water

Standard BOD test

Sample of water

1



BOD bottle

1000 ml Erlenmeyer flask by Xavax and Andrew c. Picture taken from Wikimedia licensed under Public Domain

2 Incubation for several days at 20ºC and in dark

3 Measurement of dissolved concentration of O_2 **$[DO]_f$**

$$BOD = \frac{DO_i - DO_f}{p}$$

It is filled with O_2 saturated water **$[DO]_i$**

Dilution fraction ***p***

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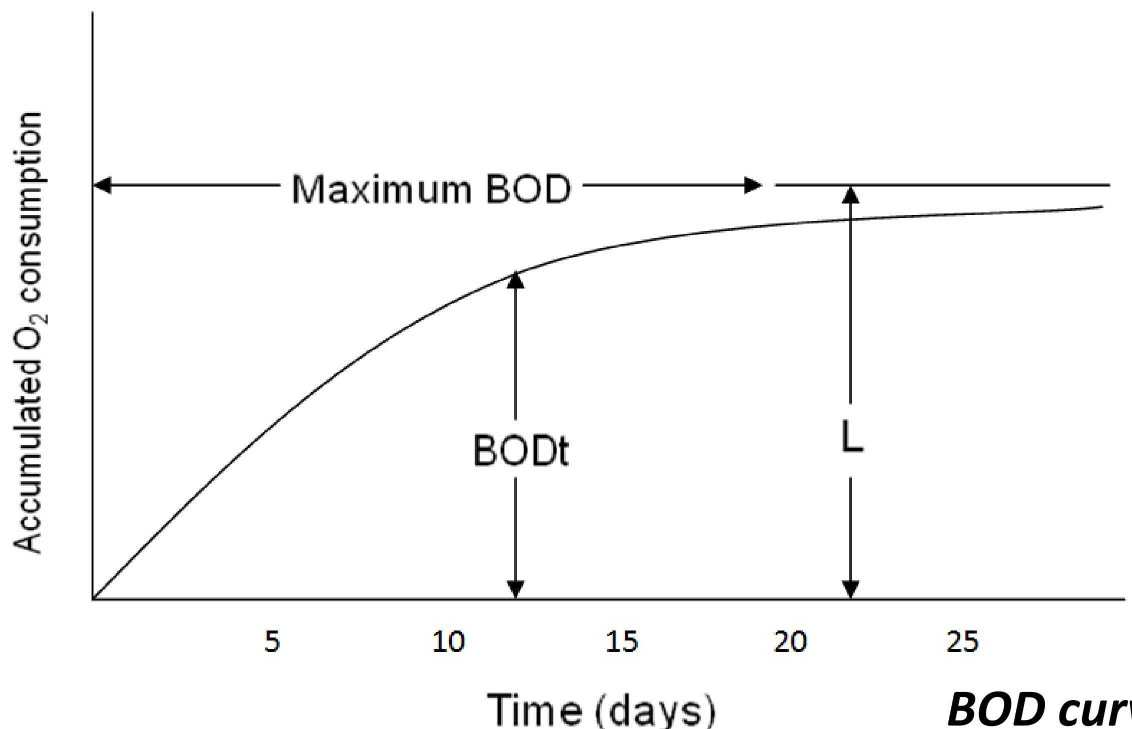
BOD curve

Biochemical oxidation is a slow process and it takes infinite time to go to completion. During the first few days the rate of **O_2 consumption** is rapid because of the high [OM] present. As the [OM] decreases, so does the rate of oxygen depletion.



BOD curve
by E. De la Torre

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BOD equation (1)

The rate of oxidation is modeled as a continuous 1st order reaction

$$\frac{\mathrm{d}L}{\mathrm{d}t} = -k\,L$$

Integration between L and BOD_t and t=0 and t=t

$$BOD_t = L\left(1 - e^{-kt}\right)$$

BOD_t = BOD exerted after time t (mg·L^{-1})

t = time (days)

L = Total or ultimate oxygen demand (mg O_2·L^{-1}) = BOD_{max}= BOD_U

k= BOD reaction rate constant (days^{-1}).

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BOD equation (2)

L or BOD_{max} expresses the concentration of biodegradable organic matter. However, it doesn't indicate how rapidly O_2 is depleted in the receiving water. This is related to the BOD reaction rate constant (*k*). The rate constant *k* varies according to

1. **Quantity and nature of organic matter (OM)**

↑ easily oxidizable OM such as glucose	↑ slowly oxidizable OM such as cellulose
↑ *k*	↓ *k*
↓ time to the BOD_{max}	↑ time to the BOD_{max}

2. **Type of microorganisms and their ability to oxidize OM**

Natural environments	Laboratory
↑ microorganisms ↑ *k*	↓ microorganisms ↓ *k*

BOD equation (3)

3. Temperature.

↑ temperature ↑ *k*	↓ temperature ↓ *k*

The reaction rate constant *k* is adjusted to the *T* of the receiving water using the following relationship

$$k_T = k_{20}\ \varphi^{(T-20)}$$

T = temperature (°C)

k_T = BOD rate constant at temperature T (days^{-1})

k_{20} = BOD rate constant at 20 °C (days^{-1})

Φ= Temperature coefficient Φ = 1.135 (T 4 - 20 °C)

Φ = 1.056 (T 20 - 30 °C)

Standard incubation period is 5 days (BOD_5). Why?

As mentioned, biochemical oxidation takes infinite time to go to completion. However, within a 20-day period, the oxidation of the carbonaceous matter is about 95-99% complete, and in a **5-day period** oxidation is from **60-70% complete** (exponential curve).

Despite the widespread use of this parameter (BOD_5), it has **some limitations**.

Attention Signal by Angel Navarro from Pixabay licensed under CC0

For the same wastewater sample (L or BOD_{max} =) BOD_5 may vary

Wastewater samples with the same BOD_5 may have a different L or BOD_{max}

BOD and COD

Although it would be expected that the value of BOD_{max} would be as high as COD, this is seldom the case.

COD ≥ BOD

... as the former includes substances that are chemically oxidized as well as biologically oxidized.

The **ratio of BOD/COD** provides a useful guide to the **proportion of biodegradable organic material** present in the wastewater.

BOD/COD ≥ 0.5 → easily treatable water by biological means

BOD/COD ≤ 0.3 → toxic components or complex compounds

NITRIFICATION

In addition to carbon, non-carbonaceous matter such as ammonia (NH_4^+) is produced during the degradation of organic matter (*e.g.* proteins).

Nitrifying bacteria are capable of oxidizing ammonia to nitrite (NO_2^-) and subsequently to nitrate (NO_3^-).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

The oxygen demand associated with the oxidation of NH_4^+ to NO_3^- is called **Nitrogenous Biochemical Oxygen Demand** (N-BOD). NBOD is influenced by the same factors as Carbonaceous Biological Oxygen Demand (CBOD).

1.4. DISSOLVED OXYGEN AND SELF-PURIFICATION

DO refers to the amount of O_2 dissolved in water.

Because it is required for respiration of aerobic microorganisms as well as other aerobic life forms, DO is one of the most important water quality parameters.

↑ DO ↑ quality water

DO <**4.0- 5.0** mg $O_2 \cdot L^{-1}$ reduction of forms of life that survive

DO > **2.0** mg $O_2 \cdot L^{-1}$ maintenance of higher life forms.

DO reflects the **self purification capacity** of the water, that is, the restoration capacity by natural processes of rivers’ or other fresh water bodies’ natural state following the introduction of a discharge of polluting material.

The most important process in self-purification is biological oxidation. However, this process does remove oxygen from solution.

$\uparrow$ Organic load

$\uparrow$ Biological activity

$\uparrow$ Oxygen demand

$\downarrow$ DO

Oxygen sources

- Re-aeration from the atmosphere.

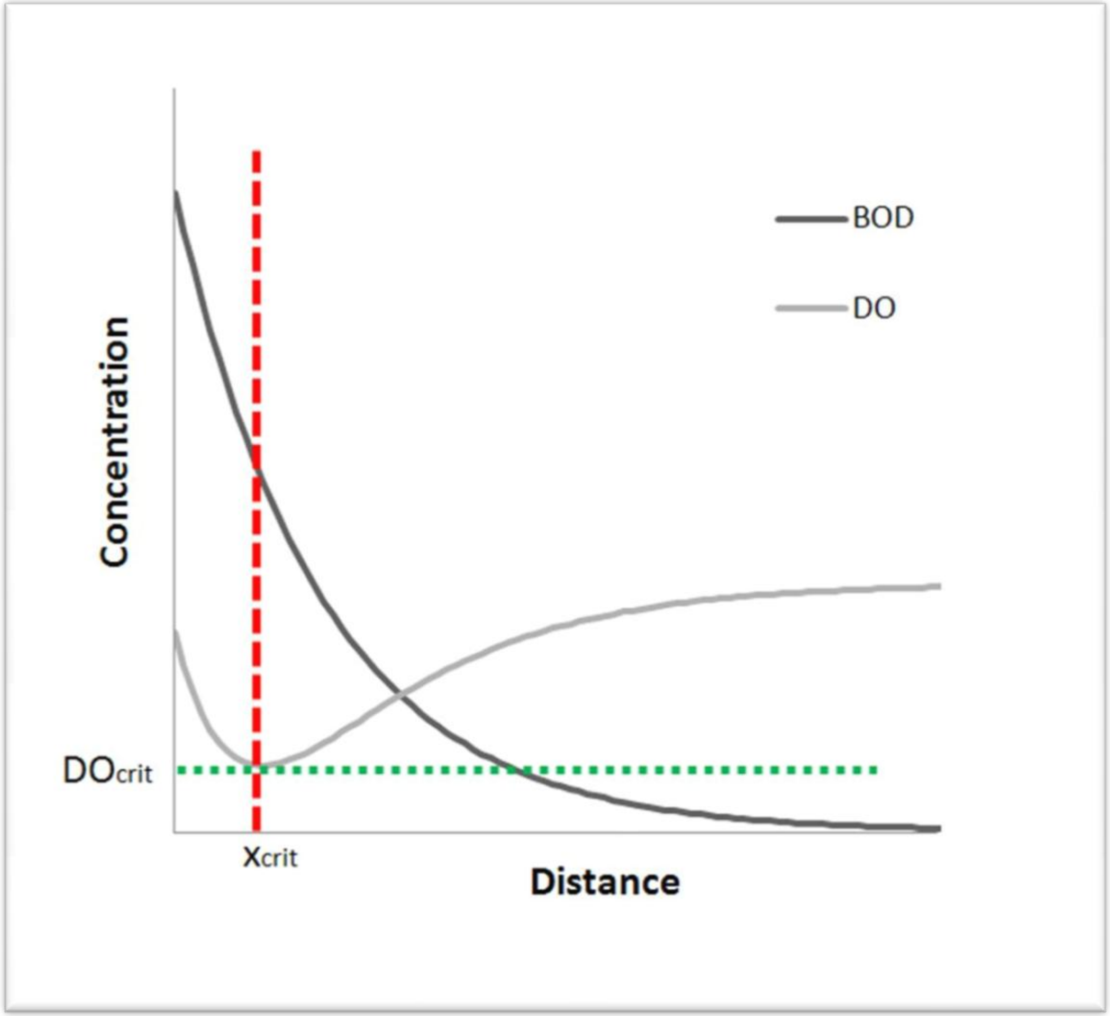
  O_2 diffuses continuously over the air-water interface in both directions. The rate of diffusion is proportional to the concentration gradient, which is described by **Fick's law.**

- Photosynthesis by aquatic plants

Oxygen sinks

- Discharges of oxygen demanding compounds
- Respiration by aquatic plants
- Respiration of organisms that live in sediments

Addition of oxidizable pollutants to streams produces a typical **oxygen sag curve** as shown in next figure.



Dissolved oxygen sag curve

"Streeter-Phelps DO sag curve and BOD development" by Emiliereiler from Wikimedia licensed under Public Domain

When an organic effluent is discharged into a stream it exerts an oxygen demand: **de-oxygenation.** This flux t is compensated by atmospheric **re-aeration**.

If the oxygen demand exceeds the oxygen transfer from the atmosphere: **initial oxygen deficit** (**D_a or D_o**). D_a is the difference between the saturation DO and DO at the point of discharge.

The variation of the **oxygen deficit** (***D***) with the distance along the stream: $D_x = \text{Saturation DO} - DO_x$

At some point downstream re-aeration ≈ de-oxygenation and the [DO] stops declining: **critical point** (***D_c***), where the oxygen deficit is greatest and the DO is lowest.

Thereafter, re-aeration predominates and the DO concentration rises to approach saturation again.

EFFECTS OF NUTRIENTS. EUTROPHICATION.

Both N and P, along with C, are essential nutrients for growth. But too much N and P in the water can cause excess algal growth. Although some algal productivity is necessary to support the food chain in aquatic ecosystems, excess growth under eutrophic conditions may lead to severe deterioration of the body of water. This is known as eutrophication, derived from the Greek word meaning 'well-nourished'.

Eutrophication

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