Water Pollution & Waste-Water Treatment

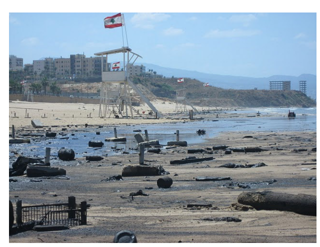
Environmental Chemistry, vanLoon & Duffy – Chapter 16

Houssam El-Rassy, PhD
Assistant Professor
Department of Chemistry, Room 520
Ext. 4051 , E-mail: Houssam.Rassy@aub.edu.lb

What is Pollution?

Water pollution is any concentration of chemicals or microorganisms in water above the "natural" level (in other words, added concentrations due to anthropogenic inputs).

A Pollutant is a substance or effect which adversely alters the environment by changing the growth rate of species, interferes with the food chain, is toxic, or interferes with health, comfort, amenities, or property values of people.



What is Pollution?

Among the criteria needed to distinguish polluted from non-polluted water, air or soils, guidelines have been established for:

1.Physical properties of temperature, color, odor and turbidity.

2. General classes of chemical properties such as pH, total dissolved solids (TSS), salinity, hardness, biological oxygen demand (BOD), detergents, and petroleum residues.

3. Specific elements, complex ions, and organic compounds.

4. Radiological properties, that is, levels of radioactivity due to particular isotopes.

5. Microbiological properties, that is, counts of specific organisms and groups of organisms.

Water Quality Guidelines – Drinking Water

Table 16.3 World Health Organization guidelines for drinking-water quality[a].

	Concentration / $\mu g\ L^{-1}$		Concentration / $\mu g\ L^{-1}$
Inorganics		Organics	
As	10	Benzene	10
B	500	Benzo(a)pyrene	0.7
Cd	3	TCE	40
CN^-	70	NTA	200
Cr	50	Pesticides	
Cu	2000	Atrazine	2
F	1500	Lindane	2
Pb	10	2,4-D	30
Mn	400	DDT	1
Hg	6	Disinfection by-products	
NO_3^-	50	Monochloramine	3000
NO_2^-	3	Dichlorobromomethane	100
Se	10	Chloroform	300

[a] From *Guidelines for drinking-water quality*, 3d edn, Chapter 8, WHO, Geneva; 2006, http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/index.html (accessed October 2009). Many other parameters are provided in this comprehensive online document along with an explanation of guideline values. Details are also provided about analytical procedures and treatment protocols. The guidelines are given in several languages.

A toxic substance is an element, compound, or microorganism that, upon exposure, creates a harmful effect on a living organism.

Toxicity applies to plants, animals, and microorganisms but the degree to which any life-form is affected by a toxic agent depends on the species and other environmental factors.

Parameters that are commonly reported as measures of toxicity are the LD_{50} and LC_{50}.

The LD_{50} is defined using this dose-response curve and is an estimate of the dose of contaminants that would be lethal to 50% of an infinitely large population of the test organism (microorganism or small mammal such as the rat).

The LC_{50} is the concentration that has a lethal effect when exposure takes place over a specific time interval).

AUB Water Quality Guidelines – Toxicity

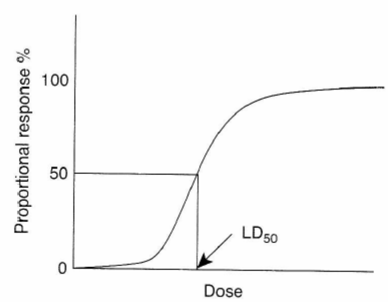


Fig. 16.1 Typical dose–response curve obtained in a toxicity test. In the case where the measured response is the death of the organism, the dose that causes death of 50% of the test population is called the LD_{50} (lethal dose 50).

For industrial and irrigation purposes, quality demands are in some ways less severe than those for drinking water.

The most important properties of water to be used for irrigation are :

- The total concentration of soluble salts.
- The molar ratio of sodium to calcium and magnesium in the water.
- The concentration of potentially toxic elements, especially boron.
- The carbonate species concentration.

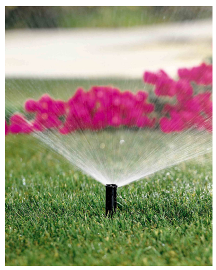


Table 16.4 Irrigation water standards for India.

Total soluble salts[a]	
Conductivity / dS m^{-1} (25°C)	Quality
<0.25	Excellent
0.25–0.75	Good
0.75–2.25	Doubtful
>2.25	Unsuitable
Sodium hazard[b]	
Sodium adsorption ratio (SAR)	Quality
<10	Excellent
10–18	Good
18–26	Doubtful
>26	Unsuitable

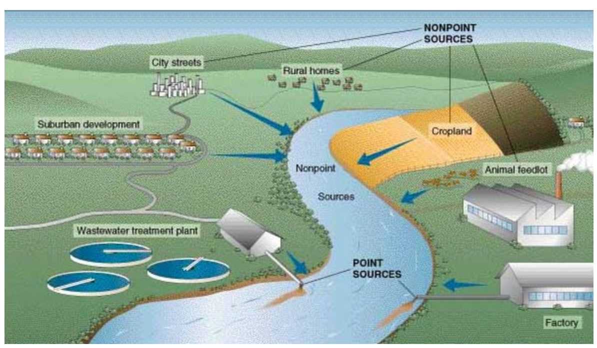
Water Quality Guidelines – Irrigation Water

Boron[c]			
Boron concentration / mg L^{-1} in crops that are			Quality
Sensitive	Semi-tolerant	Tolerant	
<0.33	<0.67	<1.0	Excellent
0.33–0.67	0.67–1.3	1.0–2.0	Good
0.67–1.0	1.3–2.0	2.0–3.0	Doubtful
1.0–1.3	2.0–2.5	3.0–3.8	Unsuitable
>1.3	>2.5	>3.8	Very toxic

Alkalinity[d]	
Carbonate alkalinity / meq L^{-1}	Quality
<1.25	Safe
1.25–2.5	Marginal
>2.5	Unsuitable

[a] Total soluble salts (salinity) are assessed by conductivity. Large concentrations of soluble salts are a contributing factor to soils themselves becoming saline. This reduces the productivity of most crops and, in the limit, makes the soil unsuitable for growth of most crops.
[b] The 'sodium hazard' is defined in terms of the sodium adsorption ratio, $C_{Na} / (C_{Ca} + C_{Mg})^{1/2}$, and is a measure of the potential of the water to saturate the exchange sites of the soil with sodium. The significance of this in terms of soil quality is described in Chapter 18.
[c] Boron is essential for normal crop growth, but is toxic when present in excessive concentrations. The sensitivity of crops is variable.
[d] Alkalinity of the water may contribute to harmful shifts in pH of the soil to the alkaline range.

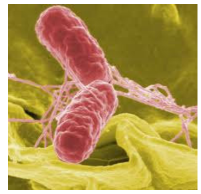
Point and Nonpoint Sources of Water Pollutants



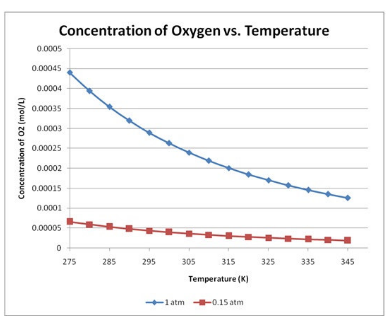
- *Point sources* discharge wastes at specific locations, usually through pipes.
  - Examples: sewage-treatment plants, factories, electric power plants, mines, and off-shore oil-drilling rigs.
- *Nonpoint sources* discharge pollutants over a wide area.
  - Examples: runoff from feedlots, cultivated land, logged forests, and construction sites.

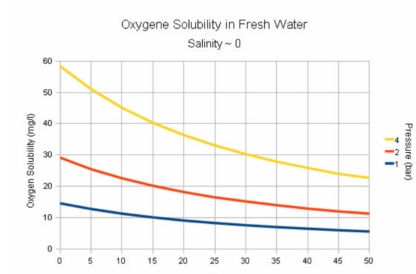
General Types of Water Pollution

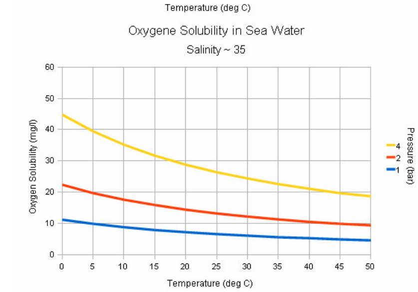
- Disease-causing agents (Pathogens)
- Oxygen-consuming agents
- Plant nutrients
- Toxic substances
  - Heavy metals
  - Pesticides
- Dissolved solids
- Acids
- Suspended solids and sediments
- Oil
- Radioactive substances (Radionuclides)
- Heat (thermal pollution)



Oxygen-Consuming Agents







Animals and plants living in an aquatic habitat depend on oxygen dissolved in the water for their survival.

The amount of dissolved oxygen (DO) depends on the temperature and the altitude.

Biological Oxygen Demand

- Energy is acquired by oxidation of organic material. In this process, oxygen is required:

  CH_2O + O_2 → CO_2 + H_2O

  12 mgC   32mg

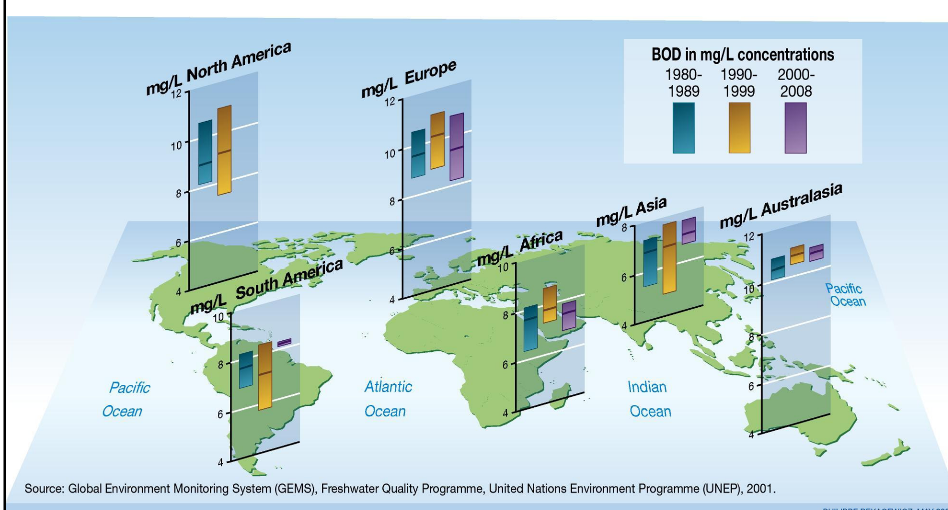
  1mgC   2.7mg O_2

- At 20°C, DO=9mg/L, therefore, only ~3.4mg of CH_2O can be oxidized by the O_2 in a liter of water.

- When the concentration of organic material is high, water can be easily depleted of DO.

- Biological oxygen demand (BOD) is the amount of O_2 (in milligram) required to carry out the oxidation of organic carbon in one liter of water.

Biological Oxygen Demand



Oxygen Consuming Wastes

- Organic waste materials released into the water can rapidly deplete dissolved oxygen.
- When water is overloaded with organic materials, oxygen-consuming (aerobic) bacteria proliferate.
- As a result, DO is consumed more rapidly than it can be replaced from the atmosphere.
- When DO < 5ppm, fish start to die.
- If DO drops further, invertebrates and aerobic bacteria will be unable to survive.
- In the absence of DO, anaerobic bacteria take over to decompose organic material → The water begins to smell unpleasant.

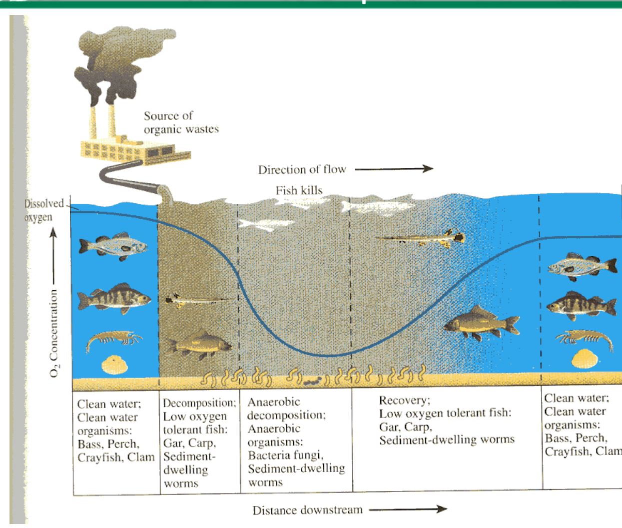
Typical BODs for Wastes from Various Processes

Type of discharge	BOD (mg O_2/liter waste water)
Domestic sewage	165
All manufacturing	200
Chemicals and allied products	314
Paper	372
Food	747
Metals	13

Decomposition Products of Organic Compounds

Element in org. compound	End products of decomposition	
	Aerobic conditions	Anaerobic conditions
Carbon	CO_2	CH_4
Nitrogen	NO_3^-	NH_3 and amines
Sulfur	SO_4^{2-}	H_2S
phosphorus	PO_4^{3-}	PH_3 and other P cmpds

Decomposition Products of Organic Compounds



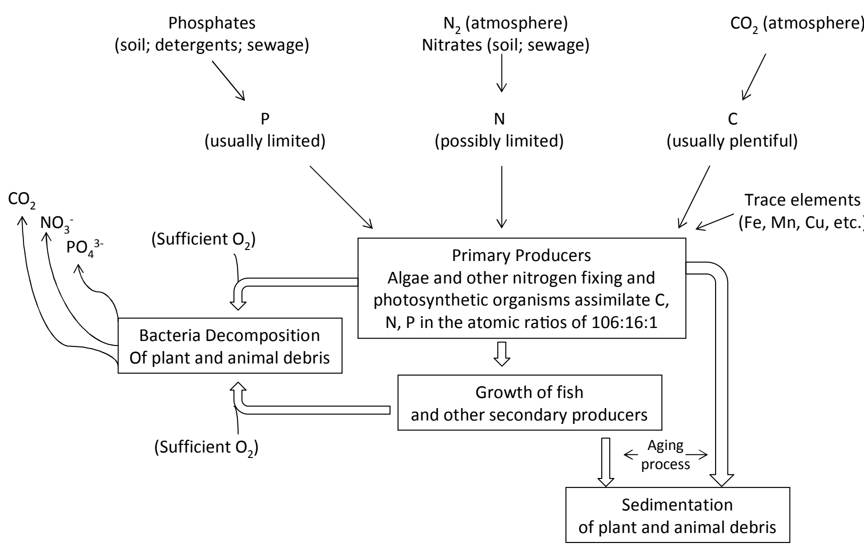
Sources of organic waste

- Human and animal sewage
- Industrial waste from paper mills, tanneries, and food-processing plants.

Plants Nutrients

- Plant growth requires various nutrients:
  - Major nutrient elements: C, N, P.
  - trace elements: S, Si, Cl, I, and metallic elements (Fe, Mn, Cu, etc).
- The minor elements, because of the low demand, can usually be supplied at adequate rates in natural waters.
- The required proportion of the major nutrient elements is C:N:P=106:16:1.
- C, despite the largest demand, is plentifully supplied to phytoplanktons from CO_2 in the atmosphere.

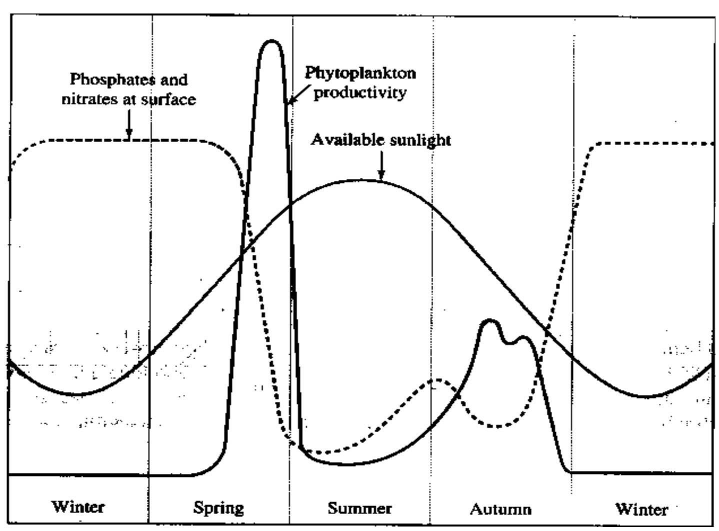
Natural Nutrient Cycling in Aquatic Ecosystem



N and P are Often the Limiting Nutrients

- The <u>limiting nutrient</u> is the least available element in relation to its required abundance.
- N is abundant in the form of N_2, but N_2 can only be utilized through N_2-fixing bacteria.
- In waters where N_2-fixing algal species are common, N is not usually limiting:
  - In regions where N_2-fixing species are less abundant, especially the oceans, N may be the limiting nutrient.
- This leaves P as the limiting element to plant growth.
- This shortage keeps the spread of vegetation under control.

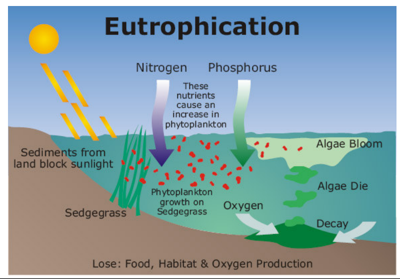
Phytoplankton Productivity as a Function of N and P Concentrations and Sunlight



Consequences of Excessive Nutrient Loading

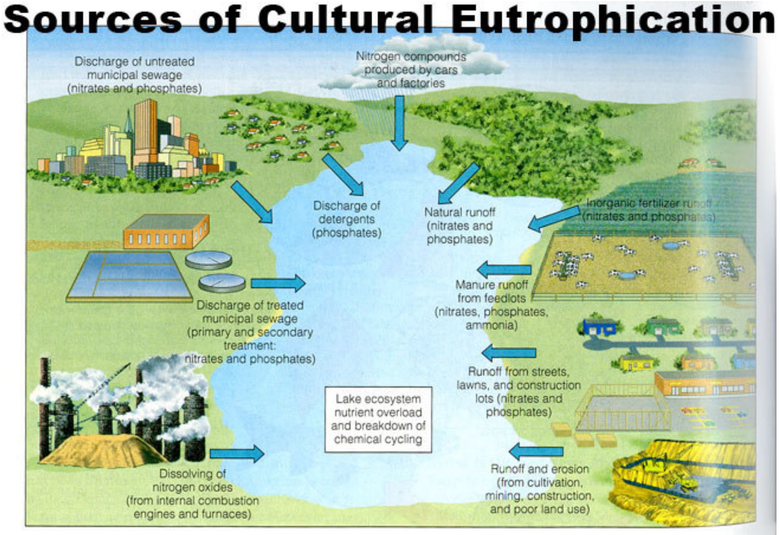
- If a *__new source__* of N or P is introduced into the water, excessive plant growth occurs, and the algae population explodes (algae bloom), this phenomenon is called *__eutrophication__*.

- Adverse consequences of eutrophication:
  - Waterways become clogged
  - Algae might release unpleasant-smelling, bad-tasting substances
  - Decay of algae induces decrease in DO.



Consequences of Excessive Nutrient Loading

Sources of Cultural Eutrophication



Sources of Nitrogen

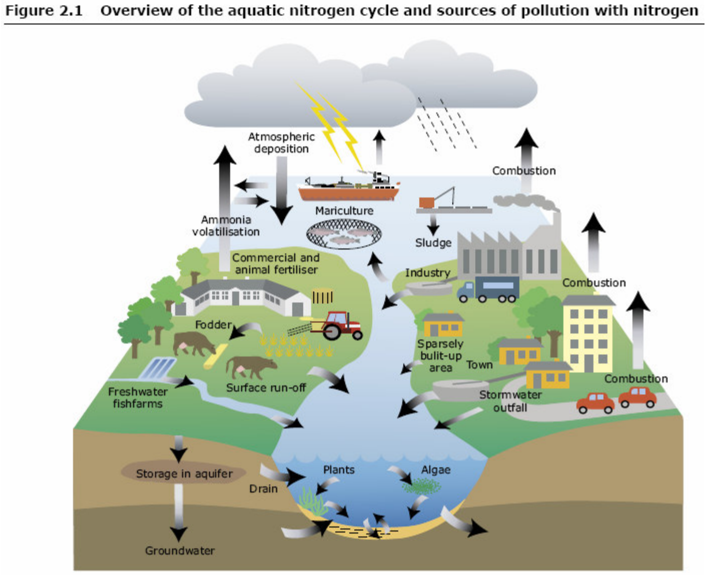
- Agriculture land treated with manure or nitrate fertilizers

- Slaughterhouses
- Stockyards

- Atmospheric deposition:
  - NO_x from automobiles, power plants, etc.

Sources of Nitrogen

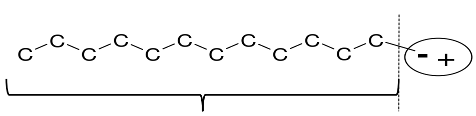
Figure 2.1 Overview of the aquatic nitrogen cycle and sources of pollution with nitrogen



Sources of Phosphorus - Detergents

- The two main ingredients in synthetic detergents are a surfactant and a builder.
- Surfactants remove grease and dirt particles from clothing and dishes by solubilizing them into water.
- Cations Ca^{2+} and Mg^{2+} precipitates surfactants in detergents, making scum.
- Builders tie up polyvalent cations and thereby prevent them from precipitating the detergents.

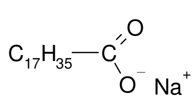
Detergents: Surfactant Structures



Long hydrocarbon tail
(oil soluble; hydrophobic)

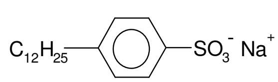
Small ionic head
(water soluble; hydrophilic)
Examples:
Carboxyl ($-COO^- Na^+$)
Sulfonate ($-SO_3^- Na^+$)
Hydroxyl (-OH)

Natural soaps-
Derived from animal fats
Example:



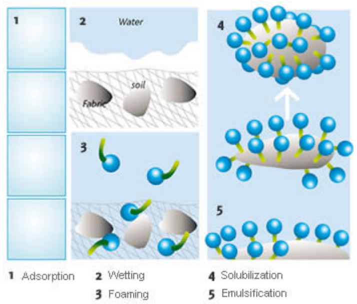
Sodium stearate

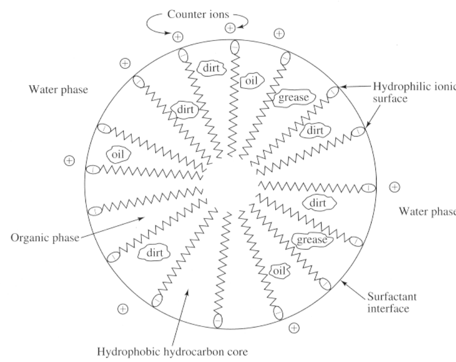
Synthetic detergents
Example:

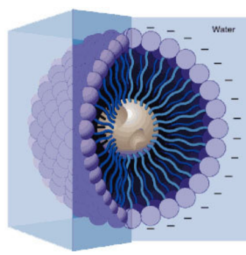


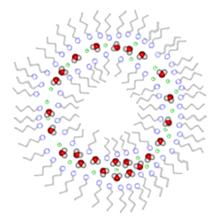
Sodium alkylbenzene sulfonate

Detergents: Surfactant Micelles





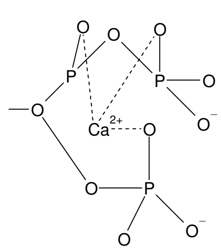


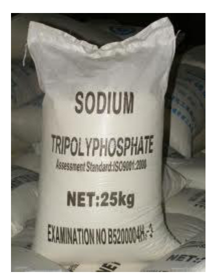


Detergents: Phosphorus-Containing Builder

Sodium tripolyphosphate (STP): $Na_5P_3O_{10}$

Ca^{2+} + STP →





Sodium tripolyphosphate serves as a builder in detergents to bind polyvalent ions.

(In addition, it furnishes the necessary alkalinity for cleaning)

Other Sources of Phosphorus

- Sewage treatment plants

- Industrial plants that use phosphorus-containing cleaning agents

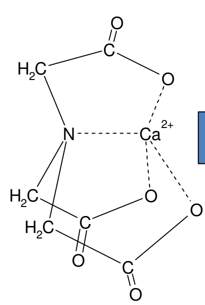
- Phosphate mines

Control of Eutrophication

- Limit discharge and atmospheric deposition of N
- Limit discharge of phosphorus-containing wastes.
  - Eradication of P in detergents

Sodium nitrilotriacetate (NTA): $N(C_2H_2O_2)_3Na_3$

Ca^{2+} + NTA →



Alternative to the P builder

The objectives for water treatment derive from two concerns:

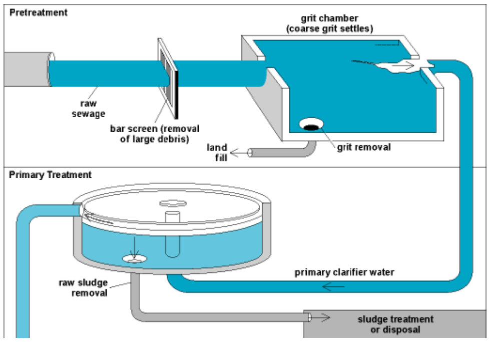
- Human health and welfare.
- The health of aquatic ecosystems.

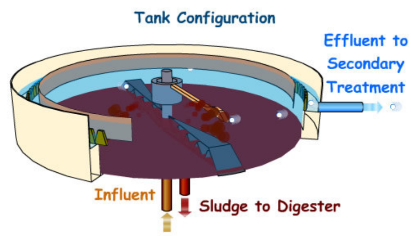
Criteria	Causing Pollutant	Corresponding removal measures
Free of odor	Odorous gases	Aeration to remove odor gases
Free of turbidity	Particles	Addition of Fe^{3+} and Al^{3+} to trap particles
Low BOD	Organic materials	Bacteria metabolism
Low nutrient loading	Dissolved N, P inorganic	Chemical precipitation NH_3 stripping
Free of disease causing agents	microorganisms	Addition of disinfectants

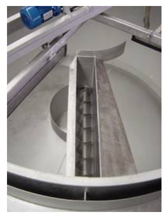
Primary treatment: Remove solids by screening and settling:

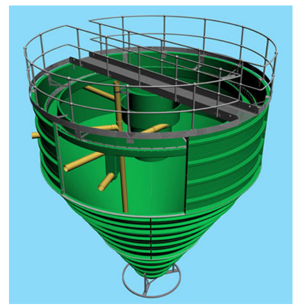
- The sewage is passed through a screen to remove large pieces of debris (e.g. sticks, stones, rags, and plastic bags).
- Next, the sewage enters a grit chamber, where the water flow is slowed just enough to allow coarse sand and gravel to settle out on the bottom.
- Water then enters the sedimentation tank, its flow rate is further decreased to permit suspended solids to settle out as raw sludge.

Primary Water Treatment









http://techalive.mtu.edu/meec/module21/CSOs.htm

Primary Water Treatment

- $Ca(OH)_2$ and $Al_2(SO_4)_3$ are often added to speed up the sedimentation process:

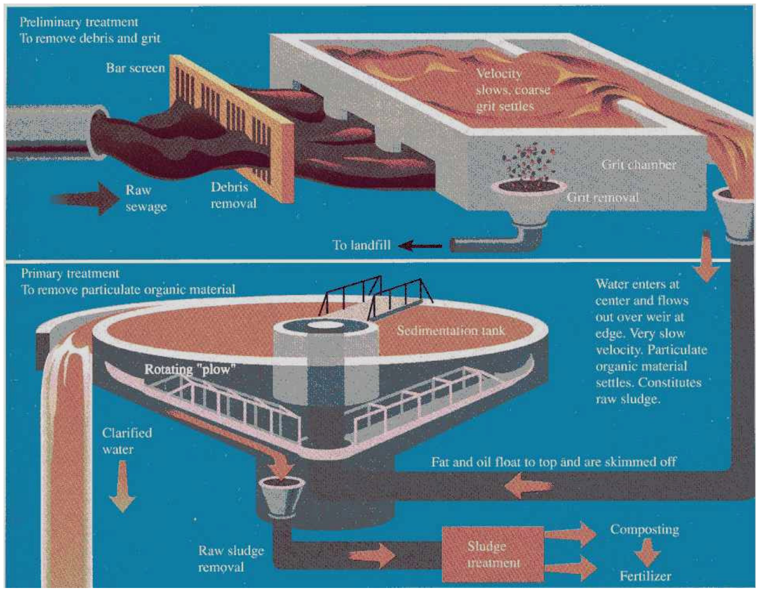
  $3\ Ca(OH)_2 + Al_2(SO_4)_3 \rightarrow 2\ Al(OH)_3 + 3\ CaSO_4$

$Al(OH)_3$ is a gelatinous precipitation that settles out slowly, carrying suspended material and bacteria with it.

- Oily material floats to the surface and is skimmed off.

- The grit is collected and disposed in landfill.

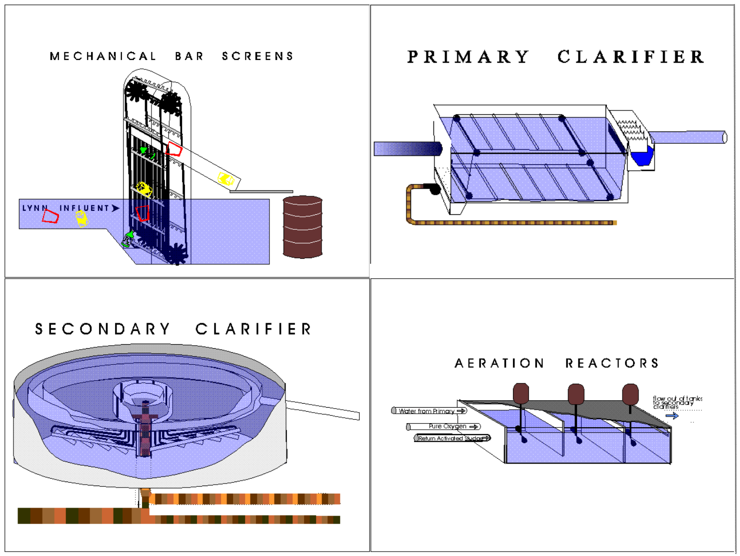
- The raw sludge:
  - Old way: incinerated, disposed in landfill or dumped at sea.
  - New way: composted to produce a nutrient-rich bacteria-free material for use as fertilizer.



• In older sewage-treatment plants, the water after primary treatment is often chlorinated to kill pathogens and then discharged into a natural waterway.

• The discharged water at this stage still contains a large amount of oxygen-consuming wastes, which may deplete dissolved oxygen in the water way and cause eutrophication.

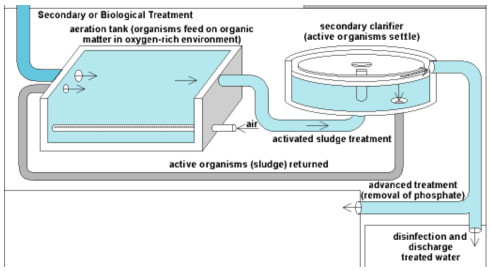
Primary Water Treatment

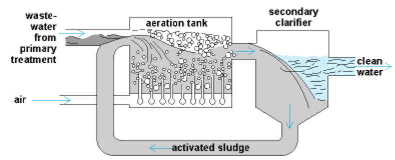


Secondary Water Treatment

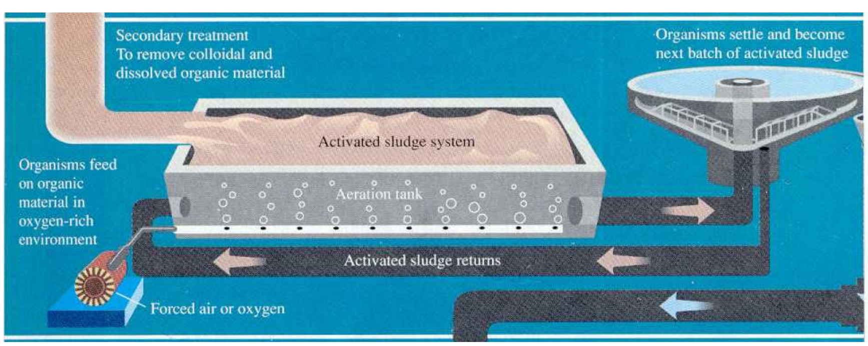
- Secondary treatment, also called biological treatment: Use bacteria to break down organic compounds to CO_2:
  - A mixture of organisms – termed activated sludge – is added to the sewage effluent.
  - Air or oxygen is vigorously bubbled through pipes into the effluent.
  - The aerobic bacteria digest the organic material and break it down into CO_2 and water.
  - The bacteria and any remaining undecomposed material are returned to the aeration tank and reused.

Secondary Water Treatment





Secondary Treatment for Municipal Wastewater



- Most municipal plants chlorinated the water after secondary treatment and then release it into waterways.

- The discharged water at this stage has ~ 90% of the original organic matter removed, but over 50% of N, P species remains, and metal ions and many synthetic organic compounds are incompletely removed.

Tertiary Water Treatment

Tertiary treatment, also called advanced waste treatment, includes a variety of processes performed on the effluent from secondary waste treatment.

- Remove P nutrients:

➢ P removal by precipitation with lime: $3\ PO_4^{3-} + CaO\ (lime) \rightarrow Ca_5(PO_4)_3(OH)$

➢ Phosphate can also be removed by microorganisms that absorb phosphate.

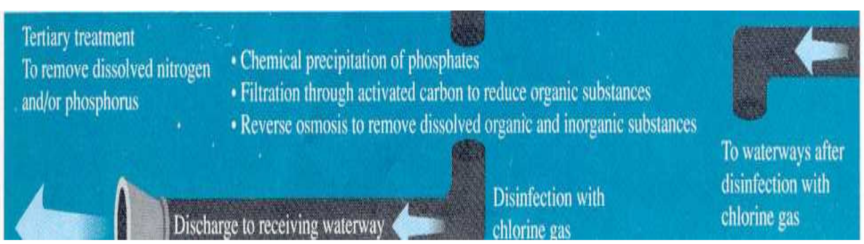
- Remove N nutrients:

➢ NH_4^+ removal by ammonia stripping:
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ (Excess OH^- from lime)

➢ Alternative NH_4^+ removal: nitrifying bacteria convert NH_4^+ to NO_3^- followed by denitrifying bacteria to convert NO_3^- to N_2.

- Remove organics through filtration by activated carbon.

Tertiary Water Treatment



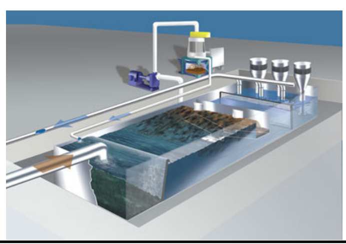
Performance of Primary and Secondary Stages of Sewage Treatment

	Pollutants Removed	
Component removed	**Primary treatment**	**Secondary treatment**
Biological oxygen demand	30%	90%
Suspended solids	60%	90%
Nitrogen compounds	20%	50%
Phosphorus compounds	10%	30%

Source: American Chemical Society

Sludge Disposal

- Sludge is an excellent fertilizer in principle: rich in organic material and nutrients.
- Sludge often contains toxic metal species, which restricts the application of sludge to cropland.
- Sludge can be a low-quality fuel for generating electricity.
- Sludge could be converted to methane by anaerobic bacteria, but this option suffers poor economics.



Disinfection

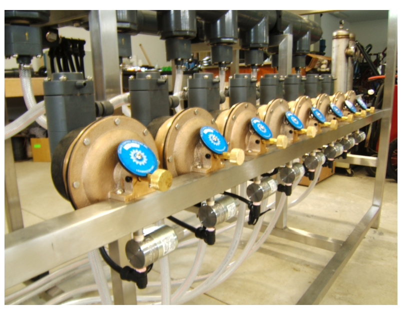
- Common disinfectants: Chlorine, chlorine dioxide, and ozone.

- Disinfectants kill microorganisms by oxidizing vital molecules (often with unsaturated carbon bond) in them.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Active disinfection component

Disinfection



AUB

Pros and Cons of Various Disinfectants

- Cl_2:
  - Cl_2 is effective and relatively cheap.
  - HOCl can act as a chlorinating agent to produce a variety of chlorinated organic compounds (for example, $CHCl_3$).
  - Many of the Cl-containing organics are toxic and non-biodegradable. Some (e.g. CH_2Cl_2, $CHCl_3$, C_2HCl_3) are suspected carcinogens.

- O_3 and ClO_2:
  - More expensive than Cl_2.
  - Need to be generated on-site → add on to the capital cost.
  - Fast-acting and rapidly decomposed. (Persistence of disinfectants allows disinfect water where leakage through old pipes occur.)

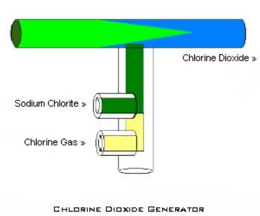
AUB

Generation of ClO_2 and O_3

- ClO_2

  $2\ NaClO_2\ (s) + Cl_2\ (g) \rightarrow 2\ ClO_2\ (g) + 2\ NaCl\ (s)$

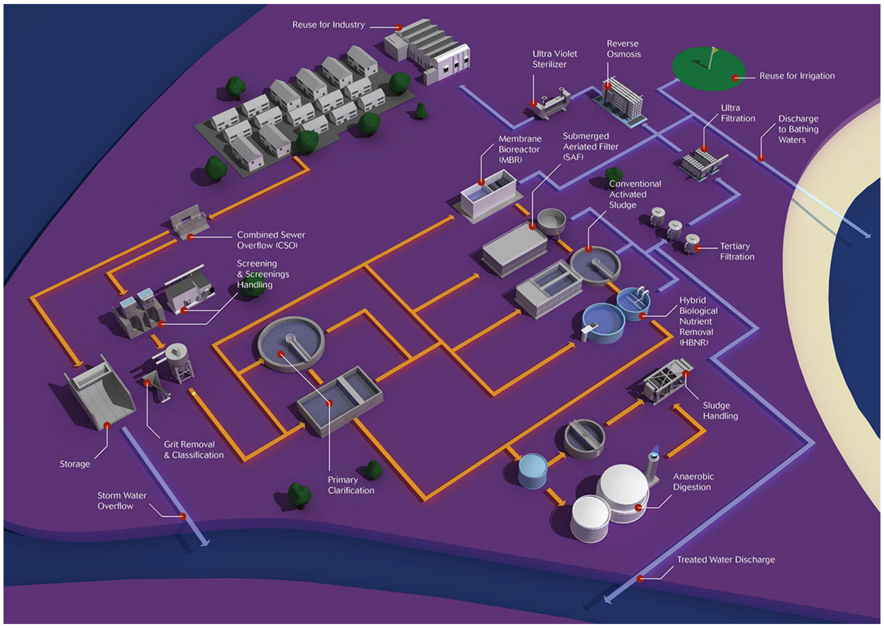
  Sodium chlorite



- O_3

  Subject pressurized air to an electronical discharge of ~20,000 Volts.

Wastewater Treatment Plants



Wastewater Treatment Plants