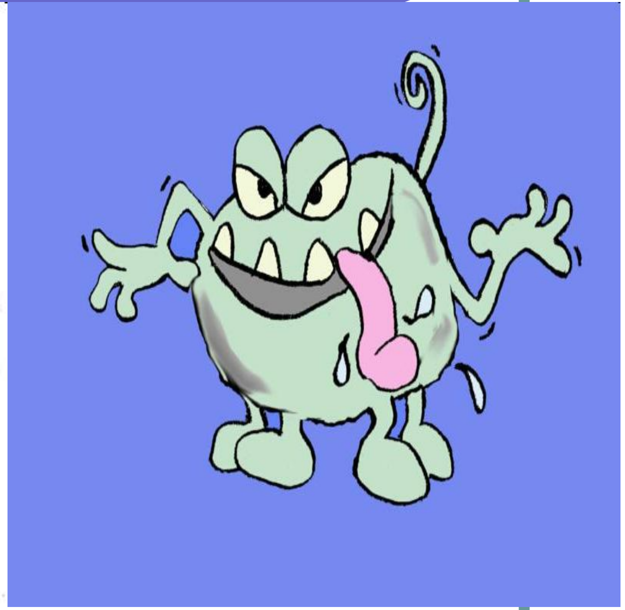
Chapter 2-Wastewater Characterization & Treatment



Raúl Muñoz
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What´s the problem???

High Content of C, N, P

O_2 depletion in Water Bodies

Eutrophication of lakes and rivers

Photo by Jess Van Dyke

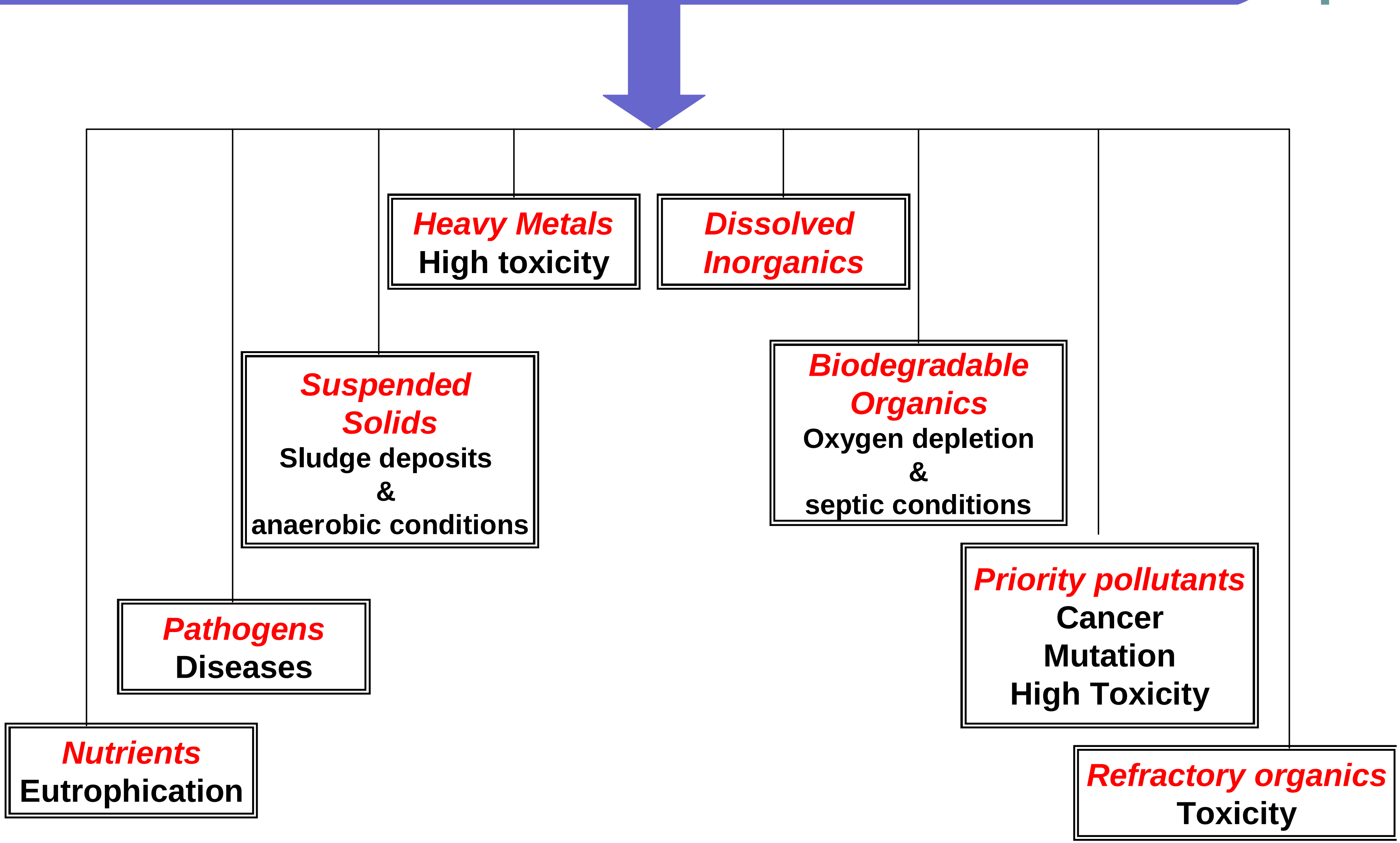
Eutrophication - an algal bloom resulting from too much nutrient from sources such as phosphorus and nitrogen in fertilizers.

HIGH TOXICITY AND CARCINOGENICITY DUE TO HEAVY METALS OR POPs

Source of wastewater

Source	Pollutants
Domestic	Organic matter (proteins, lipids, carbohydrates...), phosphorous, solids, ammonium, pathogens.
Industrial	Chemicals, Hydrocarbons...
Agricultural	Pesticides, Fertilizers
Storms	Atmospheric Depositions

Constituents of Wastewater



Pollutants in Wastewater

Class	Example
Particulate/suspended	Sand, clay
Organic matter	Sugar, proteins, synthetic chemicals…
Inorganic (nutrients)	Nitrate, nitrite, ammonium, phosphate
Biological	Bacteria, algae, viruses
Heavy metals	As, Cu, Cd, Pb, Hg
Hazardous & persistent organics	PAHs, pesticides, VOCs…

Examples of wastewaters

Typical sewage composition	
Component	mg/l
TS	300 – 1200
SS	100 – 350
TOC	80 – 290
BOD_5	110 – 400
COD	250 – 1000
Total N	20 – 85
Ammonia	12 – 50
Nitrite	0
Nitrate	0
Total P	4 - 15

Coking wastewater	
Component	mg/l
Phenol	190 - 3400
NH_4^+-N	100 - 470
Total nitrogen	110 - 530
Cyanide	5 - 25
Thiocyanate	120 - 820
COD	1200 - 4500

What are the main differences between the two effluents and the consequences on future treatment?

Examples of wastewaters

Typical Swine manure wastewater	
Component	mg/l
TS	33000
VS	22700
TOC	4000
BOD5	25000
COD	55000
Total N	5000
Ammonia	3500
Nitrite	0
Nitrate	0
Total P	1600

Wastewater composition also depends on the country!!!

Country/ constituent	BOD, g/capita·d	TSS, g/capita·d	TKN, g/capita·d	NH_3-N, g/capita·d	Total P, g/capita·d
Brazil	55–68	55–68	8–14	ND	0.6–1
Denmark	55–68	82–96	14–19	ND	1.5–2
Egypt	27–41	41–68	8–14	ND	0.4–0.6
Germany	55–68	82–96	11–16	ND	1.2–1.6
Greece	55–60	ND	ND	8–10	1.2–1.5
India	27–41	ND	ND	ND	ND
Italy	49–60	55–82	8–14	ND	0.6–1
Japan	40–45	ND	1–3	ND	0.15–0.4
Palestine[b]	32–68	52–72	4–7	3–5	0.4–0.7
Sweden	68–82	82–96	11–16	ND	0.8–1.2
Turkey	27–50	41–68	8–14	9–11	0.4–2
Uganda	55–68	41–55	8–14	ND	0.4–0.6
United States[c]	50–120	60–150	9–22	5–12	2.7–4.5

[a] Adapted from Henze et al. (1997), Ozturk et al. (1992), Andreadakis (1992), and Nashashibi and van Duijl (1995).
[b] West Bank and Gaza Strip.

Domestic Wastewaters

The main sources are: Residential areas, Commercial Districts, and Institutional or Recreational Facilities.

Flow Rates: 60- 90 % of water consumption becomes WW

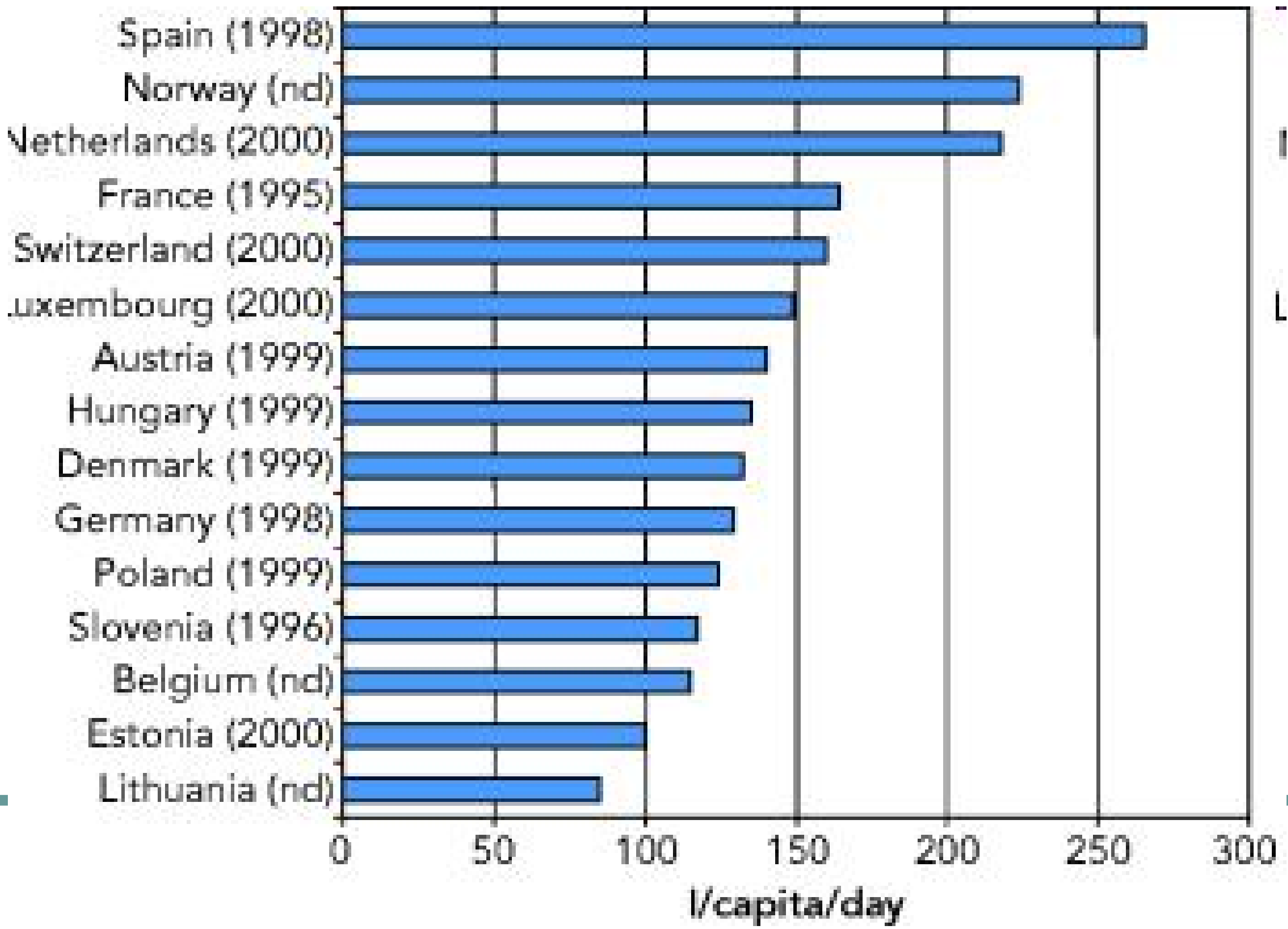
Table 3-1
Typical wastewater flowrates from urban residential sources in the United States[a]

Household size, no. of persons	Flowrate, gal/capita·d		Flowrate, L/capita·d	
	Range	Typical	Range	Typical
1	75–130	97	285–490	365
2	63–81	76	225–385	288
3	54–70	66	194–335	250
4	41–71	53	155–268	200
5	40–68	51	150–260	193
6	39–67	50	147–253	189
7	37–64	48	140–244	182
8	36–62	46	135–233	174

[a] Adapted in part from AWWARF (1999).

Domestic Wastewaters

Household water use in selected countries (l/capita/day)



Domestic wastewaters

Table 3–13
Typical unit loading factors and expected wastewater constituent concentrations from individual residences in the United States[a]

			Concentration, mg/L	
			Volume, L/capita·d (gal/capita·d)	
Constituent	**Unit**	**Typical value[b]**	**190 (50)**	**460 (120)**
BOD_5	g/capita·d	85	450	187
COD	g/capita·d	198	1,050	436
TSS	g/capita·d	95	503	209
NH_3 as N	g/capita·d	7.8	41.2	17.2
Organic N as N	g/capita·d	5.5	29.1	12.1
TKN as N	g/capita·d	13.3	70.4	29.3
Organic P as P	g/capita·d	1.23	6.5	2.7
Inorganic P as P	g/capita·d	2.05	10.8	4.5
Total P as P	g/capita·d	3.28	17.3	7.2
Oil and grease	g/capita·d	31	164	68

[a] Adapted from Crites and Tchobanoglous (1998).
[b] Data from Table 3–12, Columns 6 and 7, assuming 25 percent of the homes have kitchen waste-food grinders.

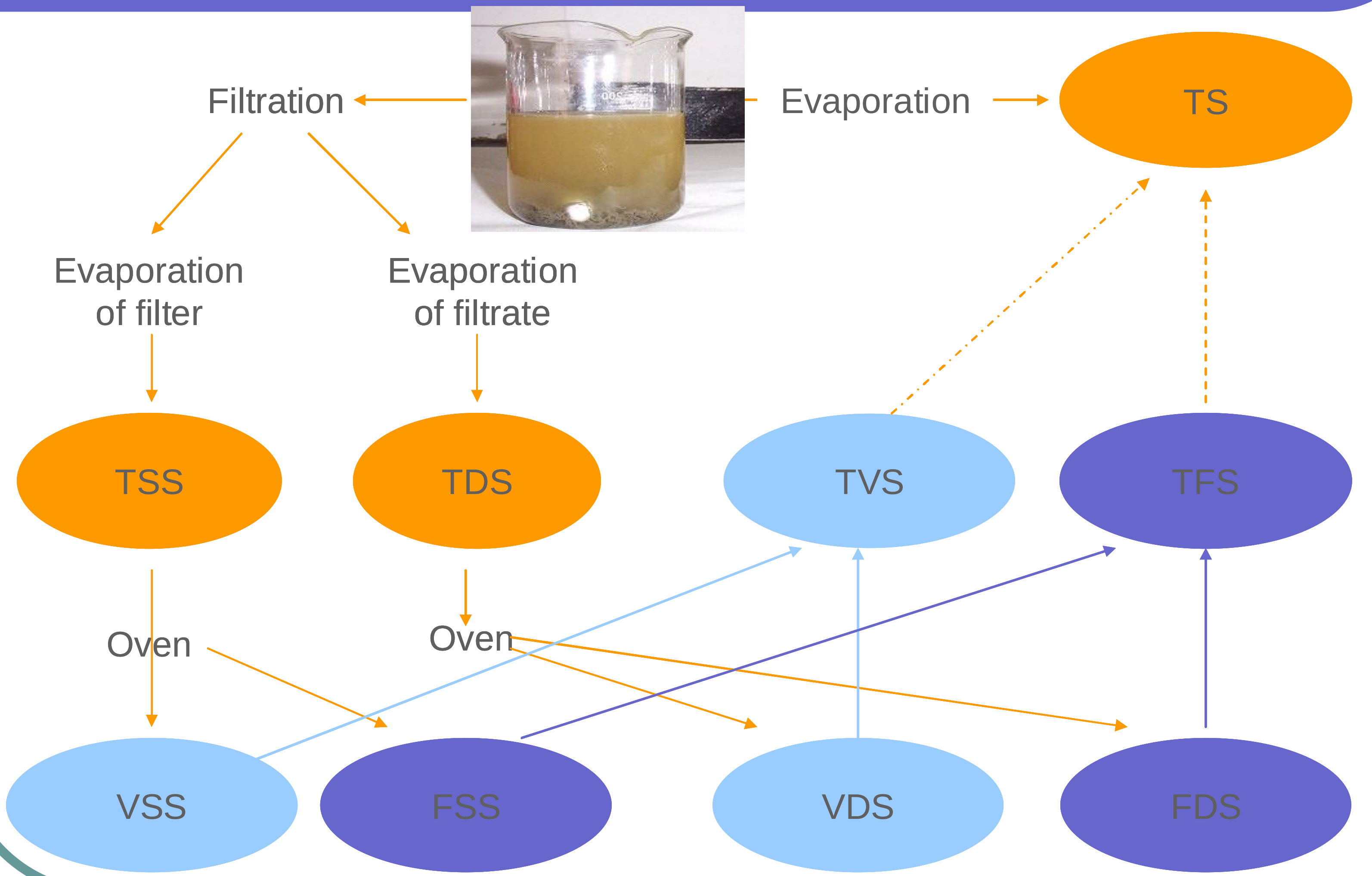
Physical characteristics

- **<u>Solids</u>** (TS, TVS, TSS, TFS, VSS, FSS, TDS...)
  - Total Solid (TS) = residue after evaporation at 103-105°C
  - TS = Total Suspended Solids (TSS >2-0.45 μm) + Total Dissolved Solids (TDS < 2-0.45 μm)
  - Total Solids = Volatile Solids (removed by ignition at 550 °C) + Fixed Solids (not removed by ignition)

- Other parameters: Turbidity (TSS), color, conductivity (TDS), temperature, sludge settleability (picture)

Imhoff cones are used to measure sludge settleability: the volume of sludge that settle after 1 h (typical. 60%)

Fractionation solids



T- Total; S- Suspended; D-Dissolved; V- Volatile; F- fixed

Why is this important to us?

- Suspended solids can be removed physically. For biomass, this allows recirculation. Soluble organic matter (VDS) is often easier to degrade than insoluble (suspended) organic matter. It is therefore important to measure the suspended fraction (that must solubilize or be hydrolyzed prior to degradation).
- **TSS** = organic-SS + inorganic-SS. The organic fraction is often considered as the **VSS**. Inert organics and inorganics take up valuable “reactor space”, influence O_2 transfer and influence the design.
- Biomass density (number of cells per unit of volume) is important because it is related to the capacity of the system. **Biomass is measured as VSS. However, VSS = active biomass + inactive VSS (dead cells, debris, etc) + other organics.**

Organic matter

Organic Matter = proteins (40-60%) + carbohydrates (25-50%) + oils & fats (8-12%) + synthetic organics. It is represented by

- **COD** = chemical oxygen demand
- **BOD** = biological oxygen demand
- **TOC** = total organic carbon
- **ThOD** = theoretical oxygen demand (calculated from the wastewater composition)

Aggregate Measurements

What are these generic parameters used for?

- Level of pollution for pollutants that cannot be monitored individually
- Process design (BOD = indication of aeration needed)

Measurements

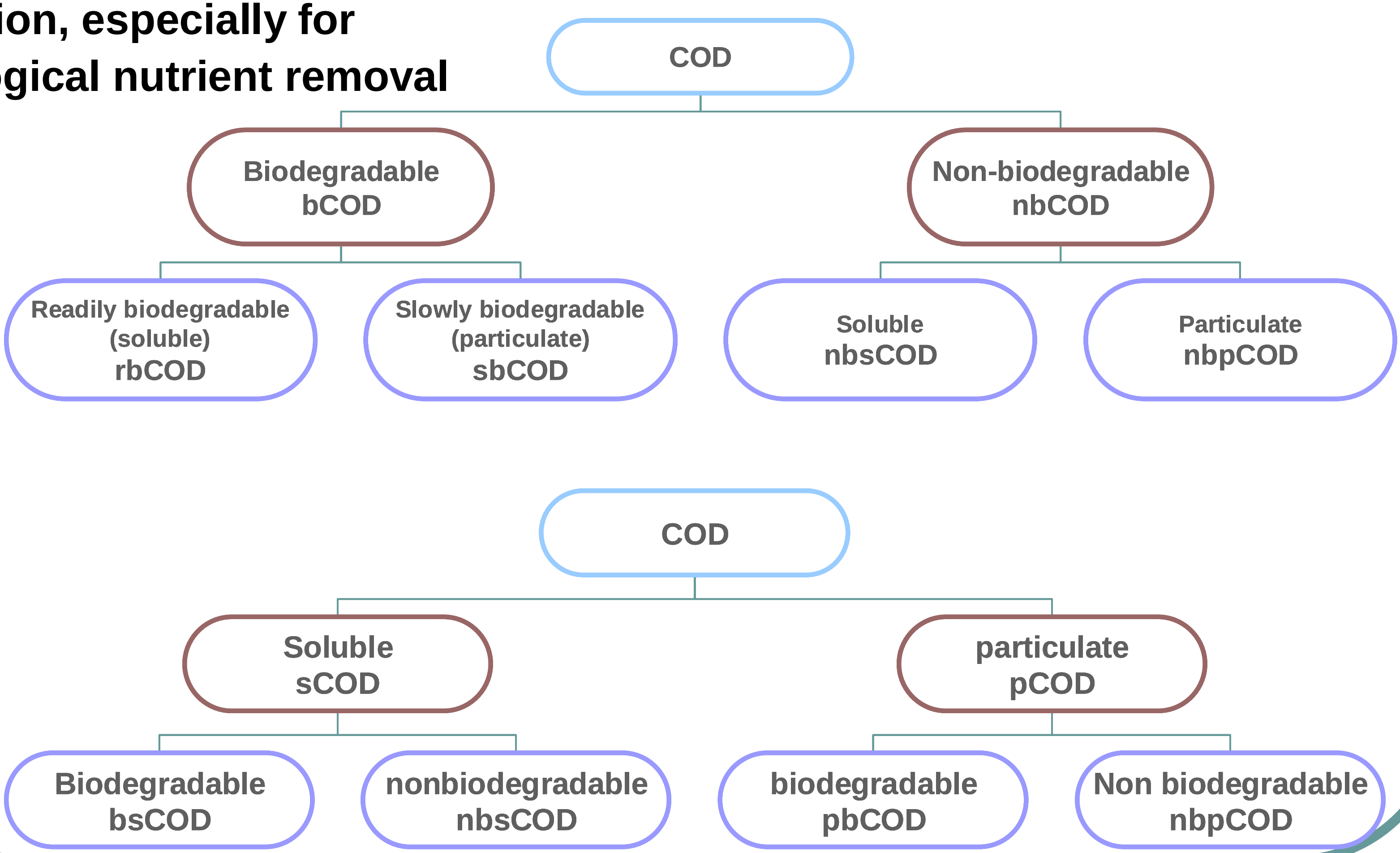
- **BOD**: A (diluted) sample of wastewater is incubated at room temperature in the dark for 5 (BOD_5) or 7 (BOD_7) days and the dissolved oxygen concentration is recorded with an electrode. If necessary, the sample is inoculated with a rich microbial inoculum (i.e. activated sludge).

- **COD:** Chemical oxidation with $Cr_2O_7^{2-}$ under acidic conditions (+ heat). Assessment by colorimetry.

- **TOC:** Measurement of organic carbon present in the wastewater.

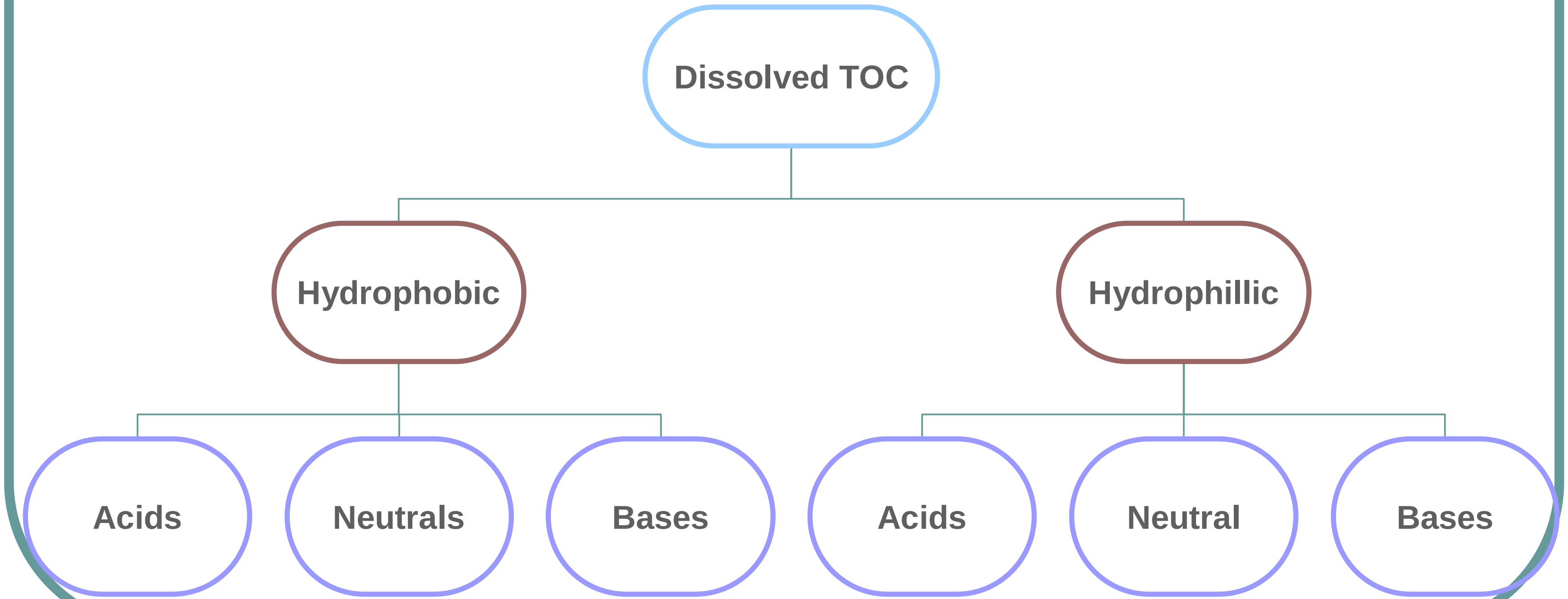
COD fractionation

The rbCOD is a very important fraction, especially for biological nutrient removal

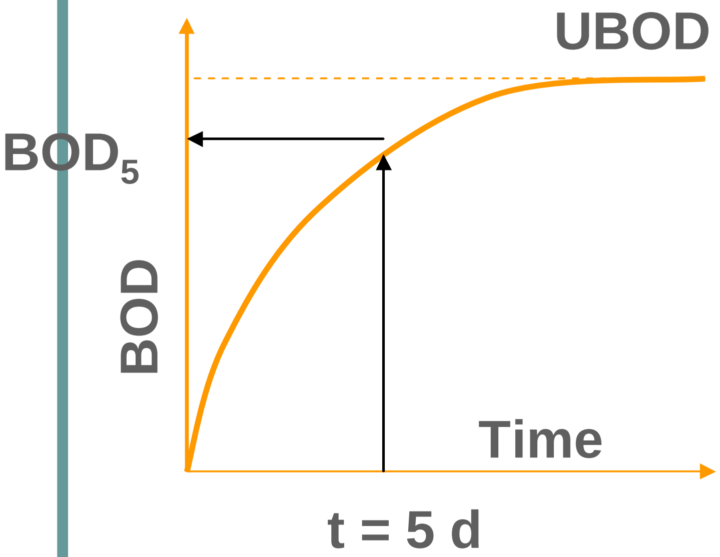


TOC fractionation

- Can also be fractionated into particulate and dissolved TOC (0.45 μm filtration)
- Can also be fractionated according the following properties:



BOD_t *vs* UBOD



BOD = biological measurement dependent on initial biological activity, type of organic matter, inherent biodegradability, toxicity and time. For domestic wastewater UBOD ≈ $1.5BOD_5$

The Ultimate BOD takes into account the oxidation of organic matter (COHNS):

$COHNS + O_2 \rightarrow C_5H_7NO_2$ (biomass) $+ CO_2 + H_20 + NH_3$ + products + heat

And the *endogenous respiration*:

$C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O$

CBOD vs NBOD

- In addition to organic matter (carbonaceous BOD or CBOD), microorganisms can oxidize ammonia to nitrite and nitrate. This results in a Nitrogenous BOD (NBOD)

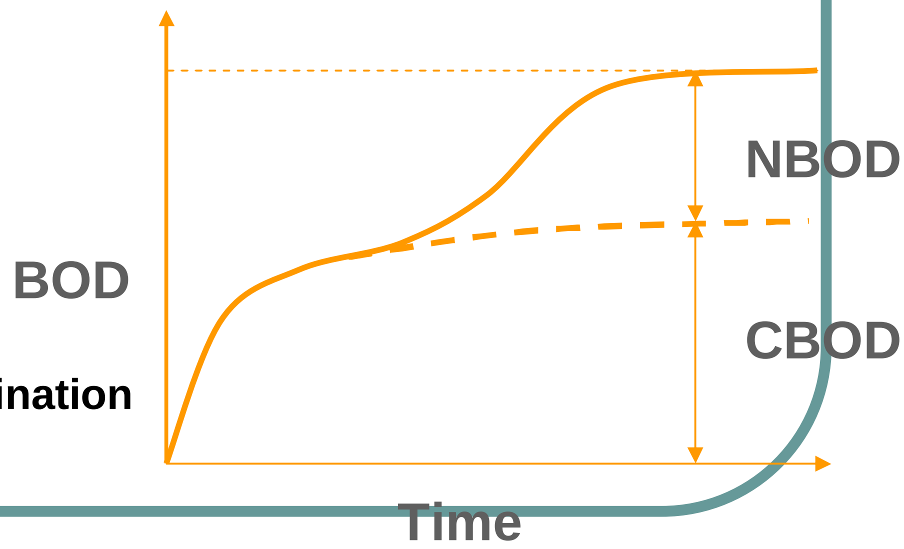
$NH_3 + 3/2O_2 \rightarrow HNO_2 + H_2O$ (*Nitrosomonas*)

$HNO_2 + 1/2O_2 \rightarrow HNO_3$ (*Nitrobacter*)

$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$

Because of the low μ of Nitrifiers, NBOD becomes important from the 6th day of incubation

Pasteurisation or chlorination-dechlorination methods suppress nitrification



ThOD

- When the wastewater composition is known, the ThOD is calculated as the amount of O_2 required to oxidize organic matter or ammonium to CO_2, NO_3^- and H_2O.
- Example: Determine the ThOD (mg) and the theoretical TOC (mg) of 1 mol of glycine ($CH_2(NH_2)COOH$)

$$CH_2(NH_2)_2COOH + {}^3\!/_2\, O_2 \rightarrow NH_3 + 2CO_2 + H_2O$$

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

$$\mathrm{ThCOD} = \left({}^3\!/_2 + 2\right)\mathrm{mol\,O_2/mol\,glycine}$$

$$3.5\ \mathrm{mol\,O_2/mol\,glycine} = 112\ \mathrm{g\ O_2/mol\,glycine}$$

Comparison

Wastewater	BOD_5/COD	BOD_5/TOC
Untreated	0.3 - 0.8	1.2 – 2.0
After primary settling	0.4 – 0.6	0.8 – 1-2
Final effluent	0.1 – 0.3*	0.2 – 0.5*

* $CBOD_5$

$BOD_5/COD > 0.5$, the waste is easily biodegradable

$BOD_5/COD < 0.3$, problem with biological treatment

Typically bsCOD = 1.6BOD

Explain?

Inorganics (N & P)

- Nitrogen can be present in many forms (NH_4^+, NH_3, NO_3^-, NO_2^-, Org-N) and certain parameters include several species (Tot-N).
- Similar for phosphate (Org-P, PO_4^{3-}, HPO_4^{2-}...)
- Other important parameters: dissolved oxygen (DO), Cl^-, pH, and alkalinity.

Nitrogen

N is a macronutrient; a building-block in protein synthesis.

Biomass is 6-10 % N. Typically biomass is represented by $C_5H_7NO_2$

N is present in several oxidation states induced by microorganisms

$$\overset{-III}{NH_3} - \overset{0}{N_2} - \overset{I}{N_2O} - \overset{II}{NO} - \overset{III}{N_2O_3} - \overset{IV}{NO_2} - \overset{V}{N_2O_5}$$

Form of nitrogen	Abbrev.	Definition
Ammonia gas	NH_3	NH_3
Ammonium ion	NH_4^+	NH_4^+
Total ammonia nitrogen	TAN	$NH_3 + NH_4^+$
Nitrite	NO_2^-	NO_2^-
Nitrate	NO_3^-	NO_3^-
Total inorganic nitrogen	TIN	$NH_3 + NH_4^+ + NO_2^- + NO_3^-$
Total Kjeldahl nitrogen	TKN	Organic N + $NH_3 + NH_4^+$
Organic nitrogen	Organic N	TKN − $(NH_3 + NH_4^+)$
Total nitrogen	TN	Organic N + $NH_3 + NH_4^+ + NO_2^- + NO_3^-$

$NH_4^+ \leftrightarrow NH_3 + H^+$

Phosphorous

P is a macronutrient; building-block in nucleic acids and cellular membrane synthesis

Biomass is 1 % P.

Type	State	Comments
Orthophosphates	PO_4^{3-}; HPO_4^{2-}, H_2PO^{4-}, H_3PO_4	Readily available for μorganisms
Polyphosphate	Several molecules of P	slow hydrolysis prior to microbial uptake
Organic Phosphate	Organically bound	Minor compound in Domestic WW

Sulphur

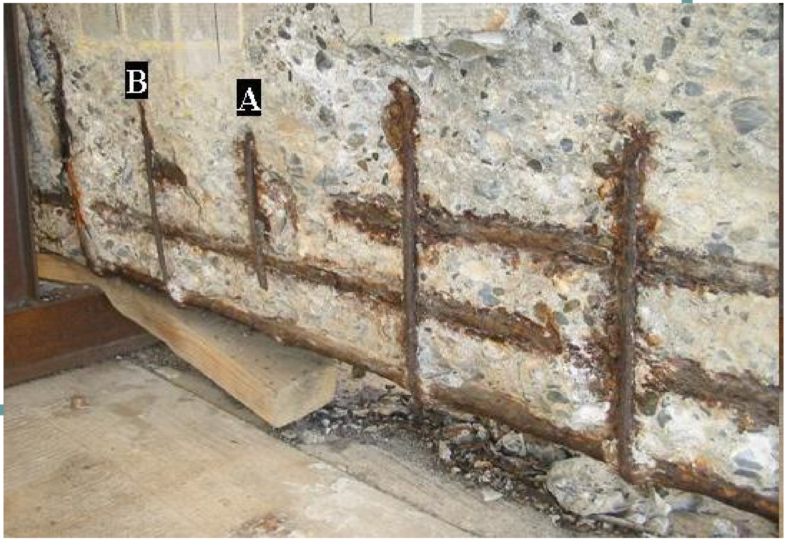
S is required for protein synthesis and released during its degradation.

In the absence of O_2 or NO_3^-:

$$\text{Organic Matter} + \text{SO}_4^{2-} \rightarrow S^{2-} + H_2O + CO_2$$

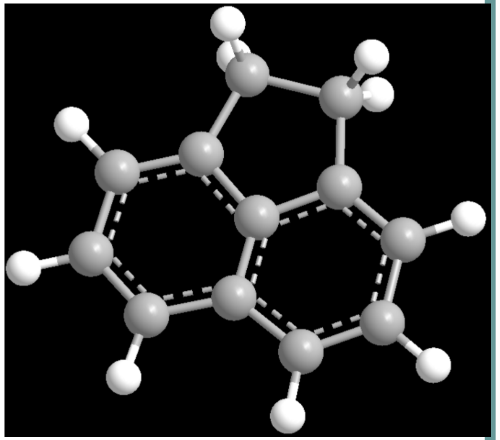
$$S^{2-} + 2H^{+} \rightarrow H_2S$$

If the H_2S stripped from the WW is oxidized to H_2SO_4 → Corrosion Problems



Heavy Metals and Priority Pollutants

Special concern and need for careful monitorization due to:



- High Toxicity
- Carcinogenicity
- Mutagenicity
- Teratogenicity

US-EPA List of priority pollutants: e.g. Benzene, lead

http://www.epa.gov/waterscience/methods/pollutants.htm

There is also an increasing concern about Emerging Pollutants: Pharmaceuticals and steroids

Pathogens

- Bacteria, Protozoa, Helminthes & viruses discharged by infected humans or animal
- Typical diseases associated are typhoid, dysentery, diarrhea and cholera
- Enumeration by direct counting, plate culture, membrane filter etc: often target a specific populations of known pathogens: the indicator organisms (i.e. E coli).
- Intensive research to develop fast methods!

Pathogens

Organism	Concentration in raw wastewater,[b] MPN/100 mL	Infectious dose, number of organisms[c]
Bacteria:		
Bacterioides	10^7–10^{10}	
Coliform, total	10^7–10^9	
Coliform, fecal[d]	10^6–10^8	10^6–10^{10}
Clostridium perfringens	10^3–10^5	1–10^{10}
Enterococci	10^4–10^5	
Fecal streptococci	10^4–10^7	
Pseudomonas aeruginosa	10^3–10^6	
Shigella	10^0–10^3	10–20
Salmonella	10^2–10^4	10^1–10^8
Protozoa:		
Cryptosporidium parvum oocysts	10^1–10^3	1–10
Entamoeba histolytica cysts	10^{-1}–10^1	10–20
Giardia lamblia cysts	10^3–10^4	<20
Helminth:		
Ova	10^1–10^3	
Ascaris lumbricoides	10^{-2}–10^0	1–10
Viruses:		
Enteric virus	10^3–10^4	1–10
Coliphage	10^3–10^4	

Pathogenic Microorganisms are few and difficult to isolate and identify → Need for the use of surrogate (indicator microorganism)

Water use	Indicator organism
Drinking water	Total coliform
Freshwater recreation	Fecal coliform
	E. coli
	Enterococci
Saltwater recreation	Fecal coliform
	Total coliform
	Enterococci
Shellfish-growing areas	Total coliform
	Fecal coliform
Agricultural irrigation (for reclaimed water)	Total coliform
Wastewater effluent disinfection	Total coliform
	Fecal coliform
	MS2 coliphage

Alkalinity

Alkalinity originates from OH^-, CO_3^{2-}, HCO_3^-, Borates, silicates, phosphates, etc.

Buffers the wastewater against sudden changes is pH

Key parameter is biological treatment systems.

$$Alk, \left[{}^{eq}\!/\!_{m^3} \right] = \left[{}^{meq}\!/\!_{L} \right] = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[OH^-\right] - \left[H^-\right]$$

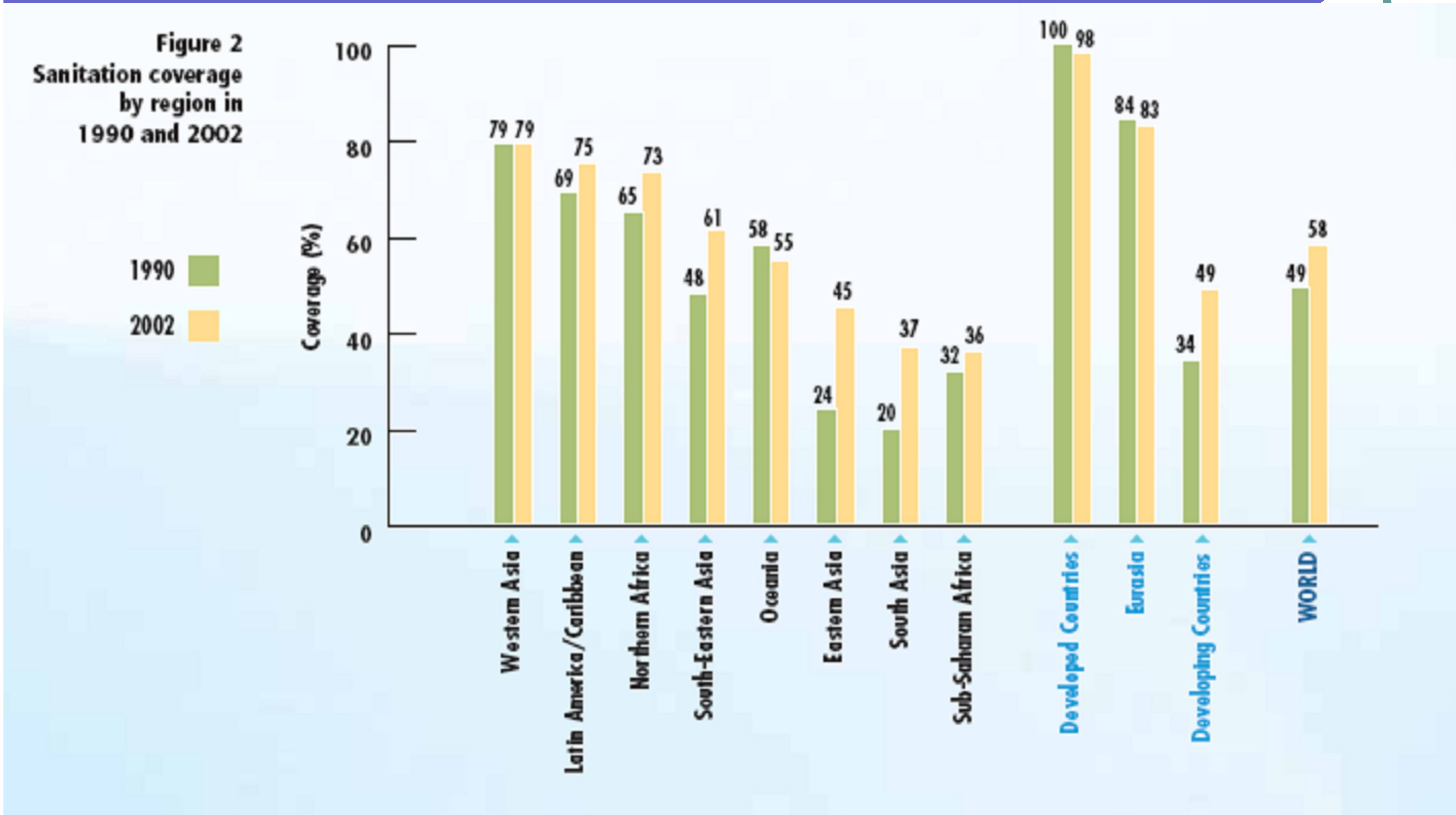
It is however usually expressed as mg $CaCO_3$ where 1 meq = 50 mg $CaCO_3$

Alkalinity is produced and consumed during WW treatment

Toxicity

- Classified according duration (short term, long term), method (static, flow through)
- Common test organisms include *Selenastrum capricornulum* (freshwater algae) and fathead minnow (fish)
- Common terms:
  - o Effective concentration (EC) or dose (ED), i.e. 48h-EC50
  - o Lethal concentration (LC) of dose (LD)
  - o Lowest observed effect concentration (LOEC)
  - o Non observed effect concentration (NOEC)

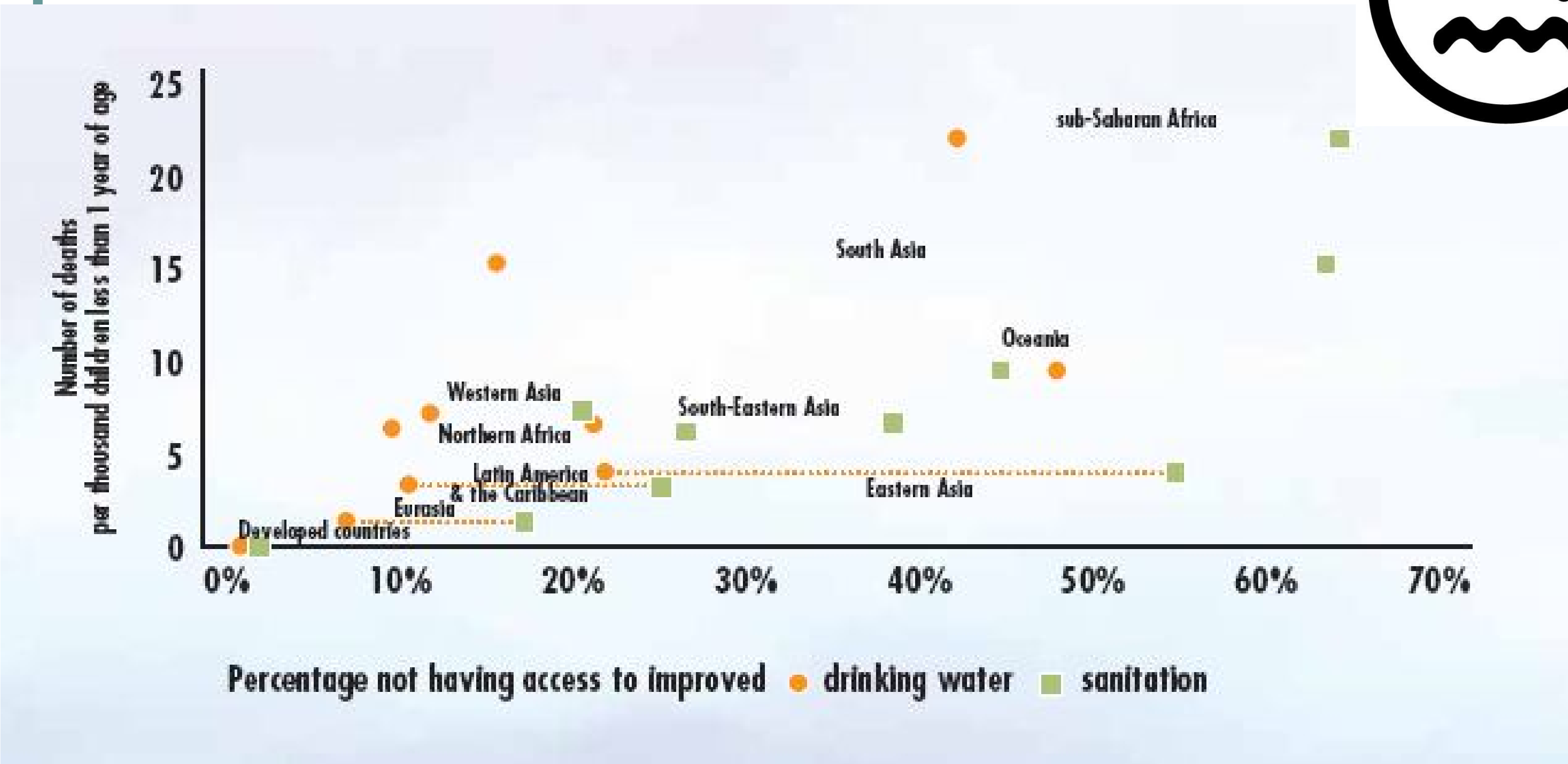
Water sanitation and Morbidity



(WHO and UNICEF, 2005: http://www.unicef.org/wes/files/JMP_2005.pdf)

Water sanitation and Morbidity

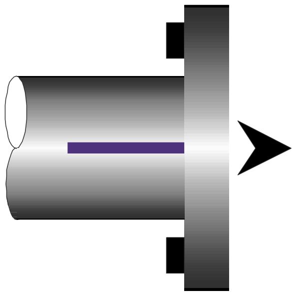
2.6 Billion People lack sanitation facilities in the world!!!



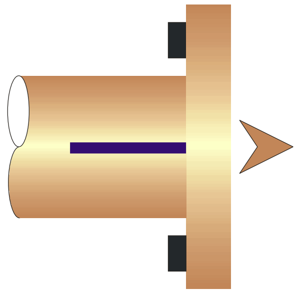
(WHO and UNICEF, 2005: http://www.unicef.org/wes/files/JMP_2005.pdf)

In BioWin 3

COD Influent



BOD Influent



- **Two Types of input: Constant Flow and Composition vs User Scheduled**
- **BioWin 3.0 allows you to load influent files**
- **Variables specified: Flow rate, Total COD, TKN, TP, Nitrate, pH, Alkalinity, Inorganic SS, Ca^{2+}, Mg^{2+}, Dissolved O_2**

In BioWin 3

WasteWater Fraction

Name	Description
F_{bs}	Fraction of total influent COD which is readily biodegradable [(S_{bsc} + S_{bsa}) / Total influent COD]
F_{ac}	Fraction of readily biodegradable COD which is VFAs [S_{bsa} / (S_{bsa}+S_{bsc})]
F_{xsp}	Fraction of slowly biodegradable influent COD which is particulate [X_{sp} / (X_{sc} + X_{sp})]
F_{us}	Fraction of total influent COD which is soluble unbiodegradable
F_{up}	Fraction of total influent COD which is particulate unbiodegradable
F_{na}	Fraction of influent TKN which is ammonia
F_{nox}	Fraction of influent biodegradable organic nitrogen which is particulate
F_{nus}	Fraction of influent TKN which is soluble unbiodegradable
F_{po4}	Fraction of influent TP which is phosphate
F_{upN}	The N:COD ratio for the influent particulate unbiodegradable COD
F_{upP}	The P:COD ratio for the influent particulate unbiodegradable COD

In Biowin 3

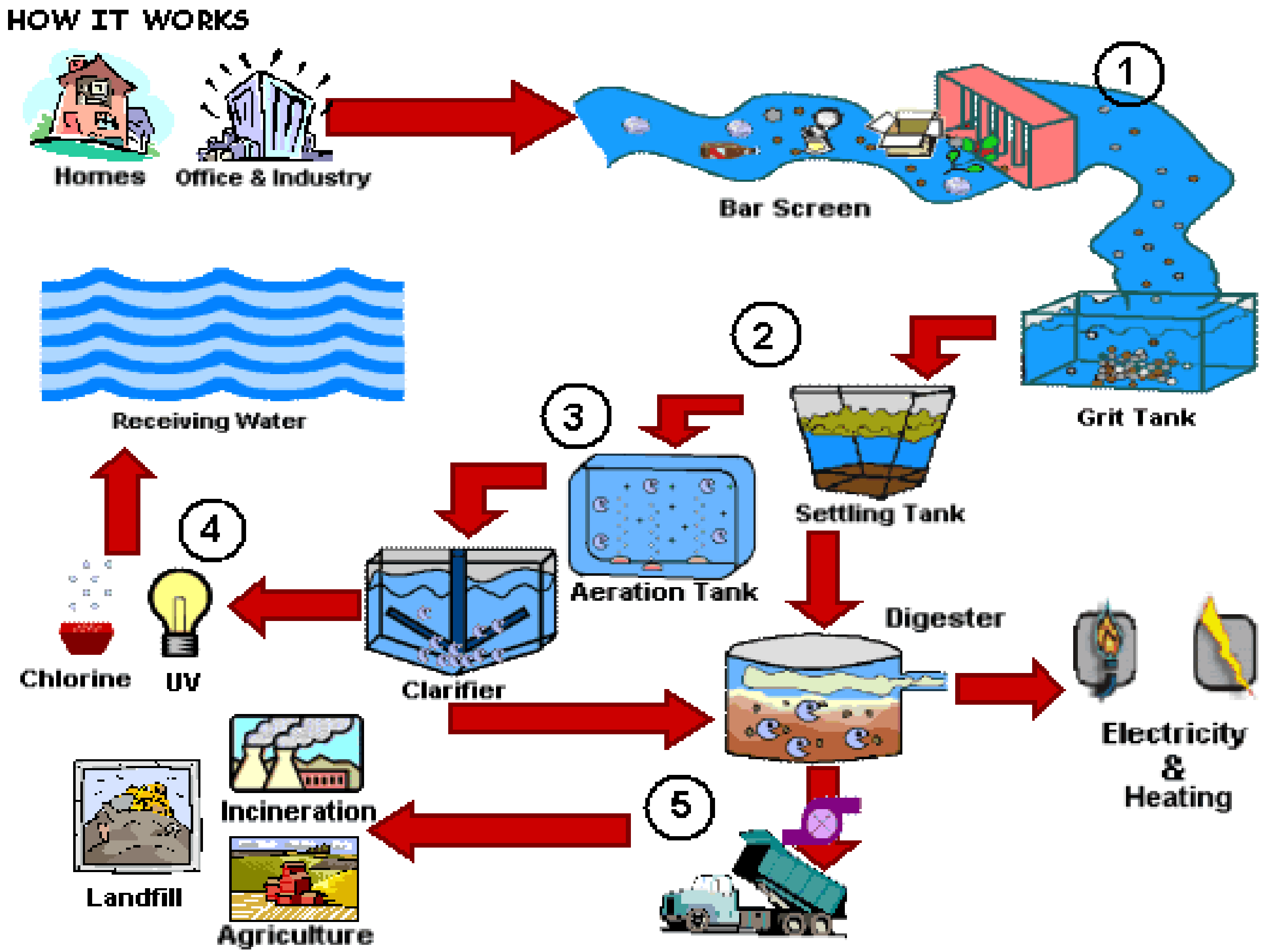
WasteWater Fraction

Name	Description
FZ_{bh}	Fraction of total influent COD which is non-polyP heterotrophic organisms.
FZ_{ba}	Fraction of total influent COD which is autotrophic organisms.
FZ_{aob}	Fraction of total influent COD which is ammonia oxidizing organisms.
FZ_{nob}	Fraction of total influent COD which is nitrite oxidizing organisms.
FZ_{amob}	Fraction of total influent COD which is anaerobic ammonia oxidizing organisms.
FZ_{bp}	Fraction of total influent COD which is polyP heterotrophic organisms.
FZ_{bpa}	Fraction of total influent COD which is propionic acid acetogen organisms.
FZ_{bam}	Fraction of total influent COD which is acetoclastic methanogen organisms.
FZ_{bhm}	Fraction of total influent COD which is H_2-utilizing methanogen organisms
FZ_{bm}	Fraction of total influent COD which is anoxic methanol utilizing organisms

Introduction to Wastewater treatment

- ✓ What are the main steps involved?
- ✓ Where are biological processes used?
- ✓ What are the challenges?

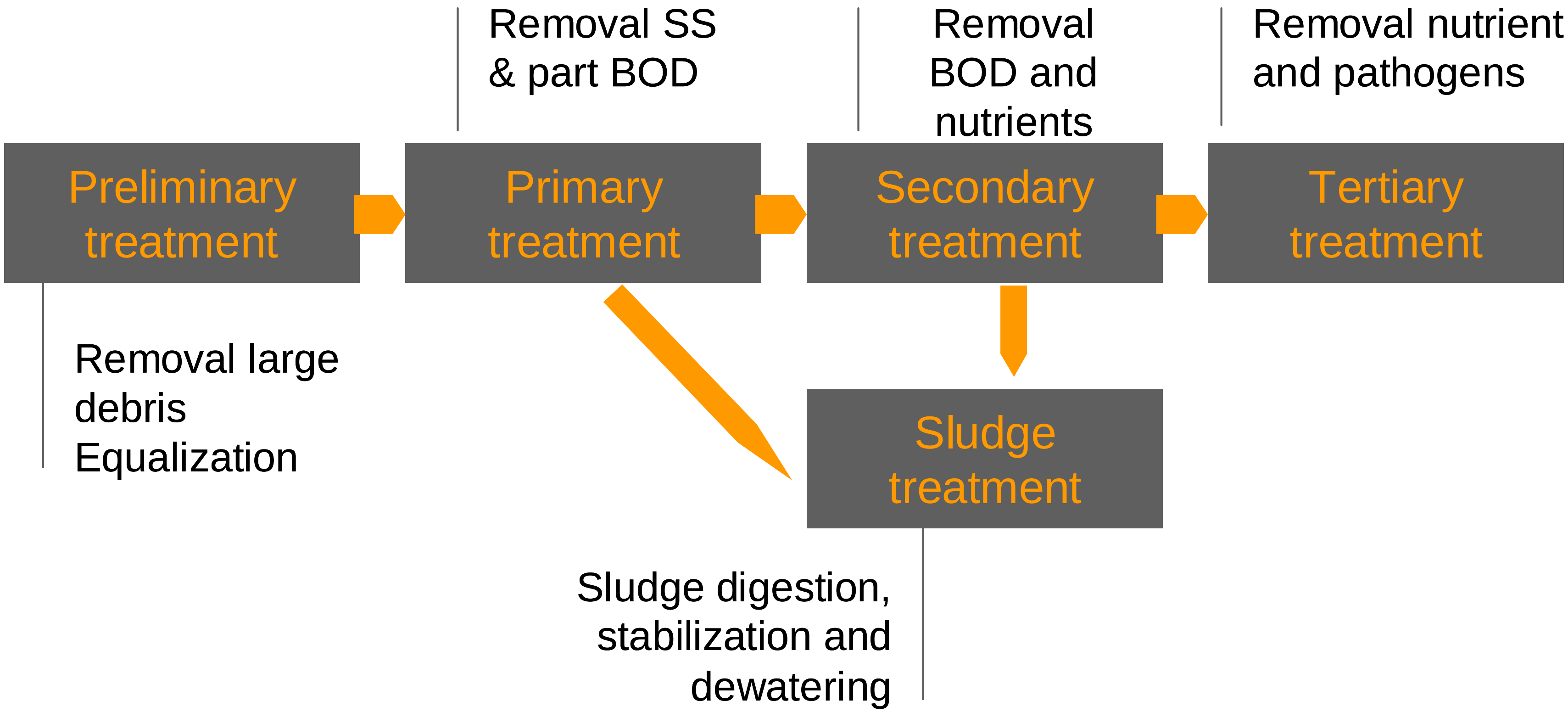
Example: City of Toronto WWTP



Mechanisms of pollutant removal

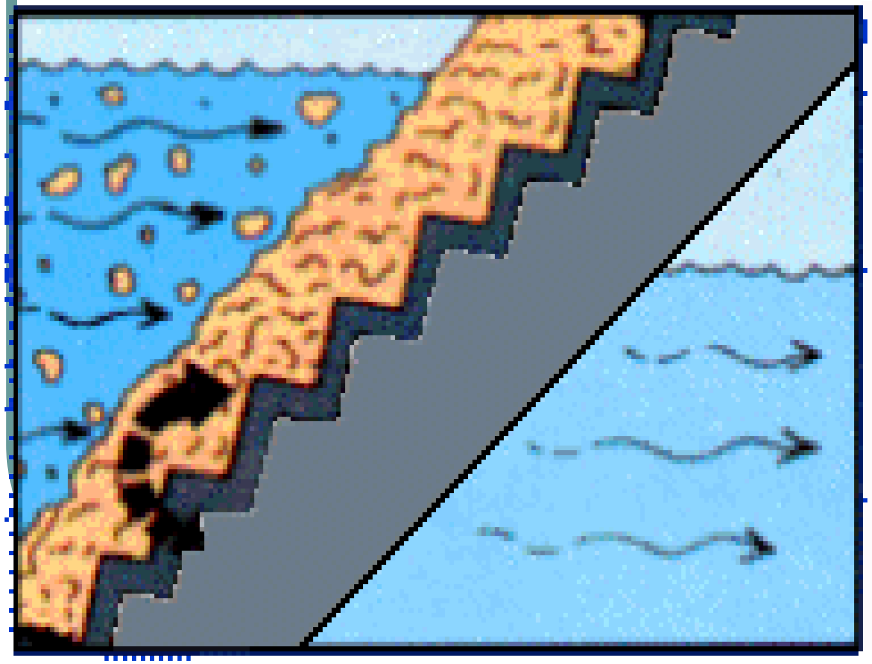
Mechanism	Pollutants affected
Adsorption/desorption	Heavy metals, trace organics
Microbial activity (including photosynthesis)	Mainly organic matter & nutrients, but also heavy metals, trace organics & pathogens
Chemical reactions (hydrolysis, photolysis, oxidation, reduction)	Organic matter, pathogens, nutrients
Filtration	TSS
Sedimentation	TSS
Flocculation	TSS
Volatilization	VOC, NH_3, CH_4, H_2S…

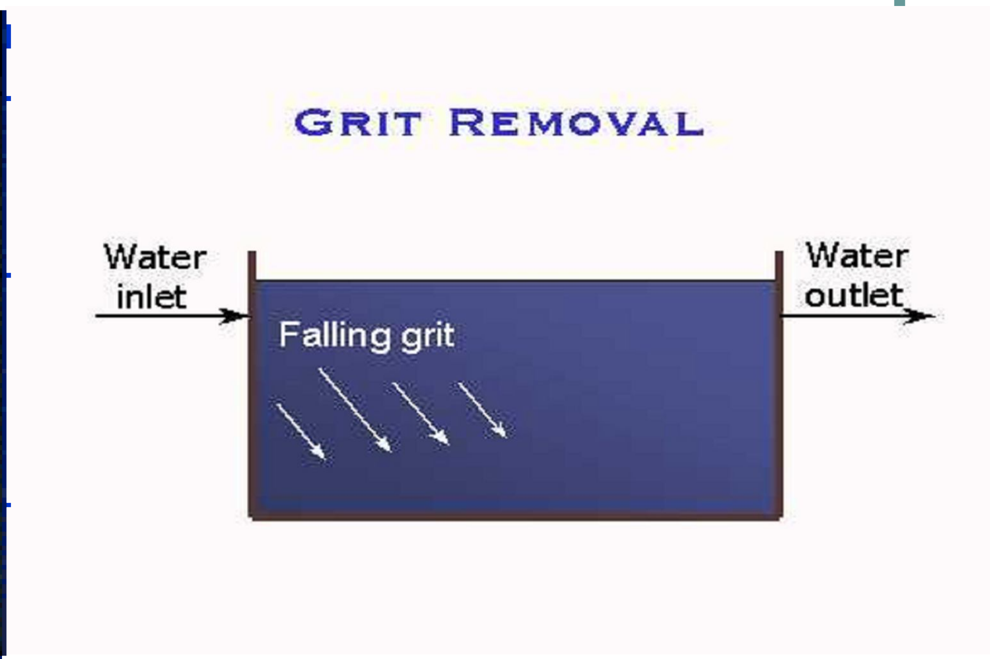
Simplified Model



Preliminary Treatment

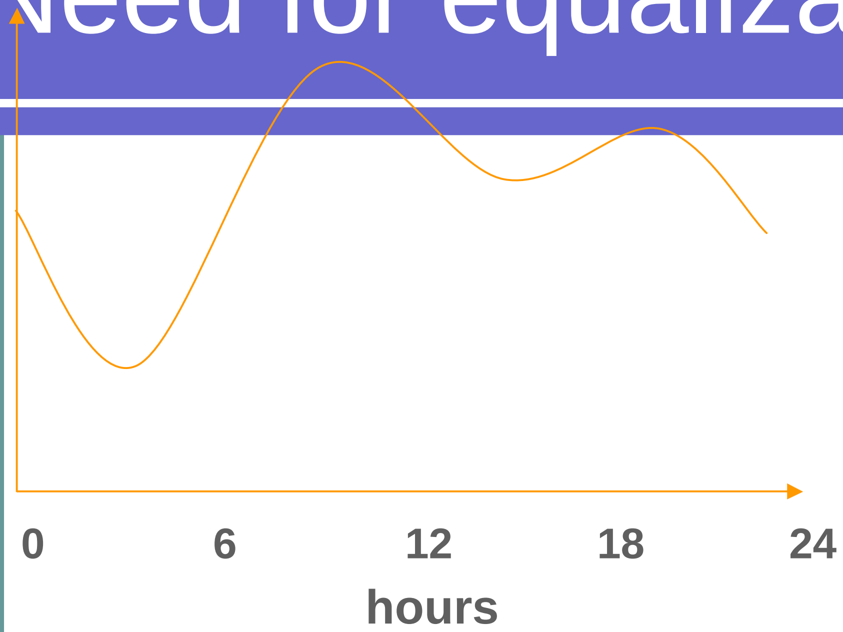
- Removal of large (screens) and heavy (grit) solids
- Equalization tank to avoid fluctuations and provide gravity forces



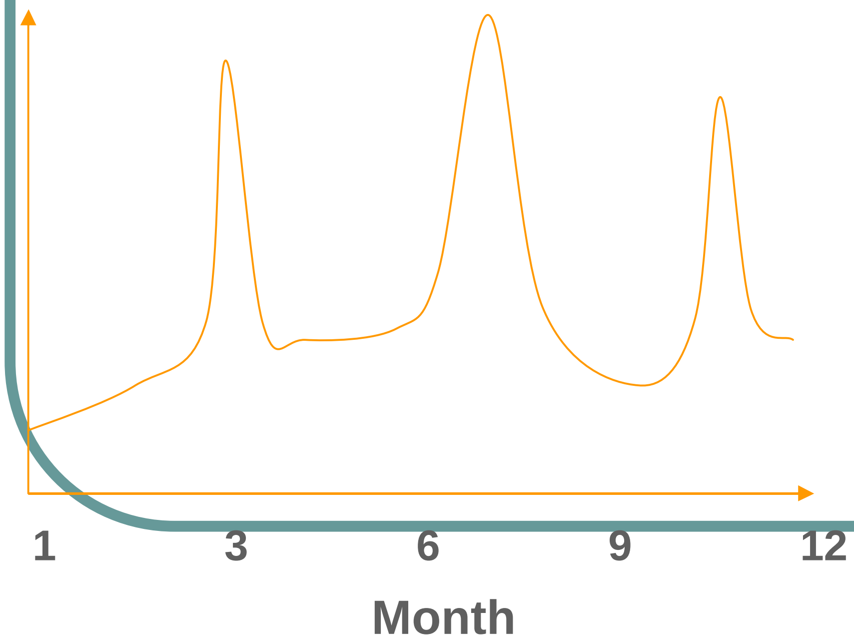


Examples: Screening

Need for equalization



Typical daily variation of municipal wastewater: User peaks during morning and evening are seen with a 1-2 hours delay at the WWT



Typical yearly variation of municipal wastewater in South France: Winter peaks reflect storms and summer peaks reflect the increase of population (up to 100 times)!

Equalisation tank

☺ Biological Treatment is enhanced because shock loadings are eliminated, pH stabilized and inhibiting substances diluted

☺ Enhanced effluent quality and secondary settler performance

☺ Surface area in filtration processes is reduced

☺ Higher efficiency in chemical treatment processes

☻ Large land areas needed

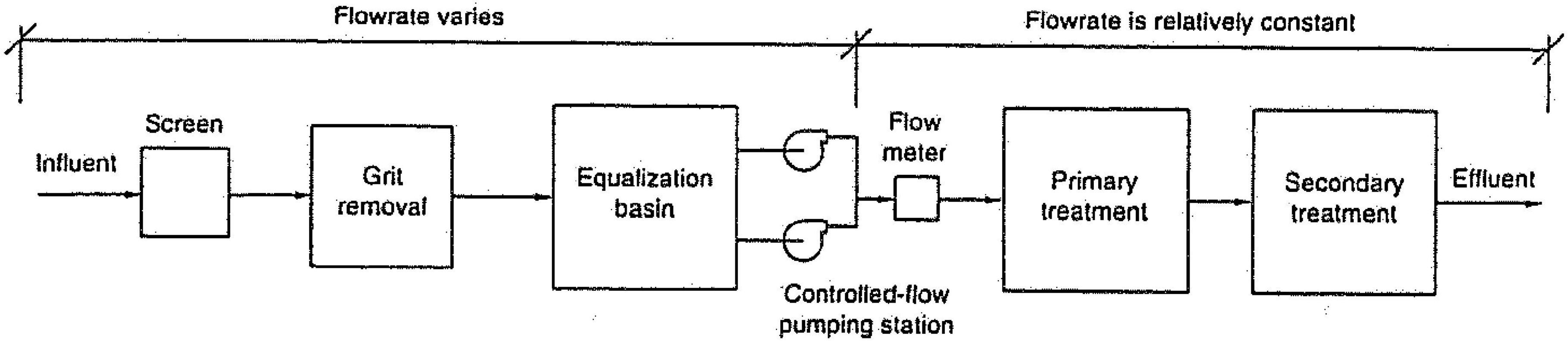
☻ Odour problems

☻ Additional Maintenance

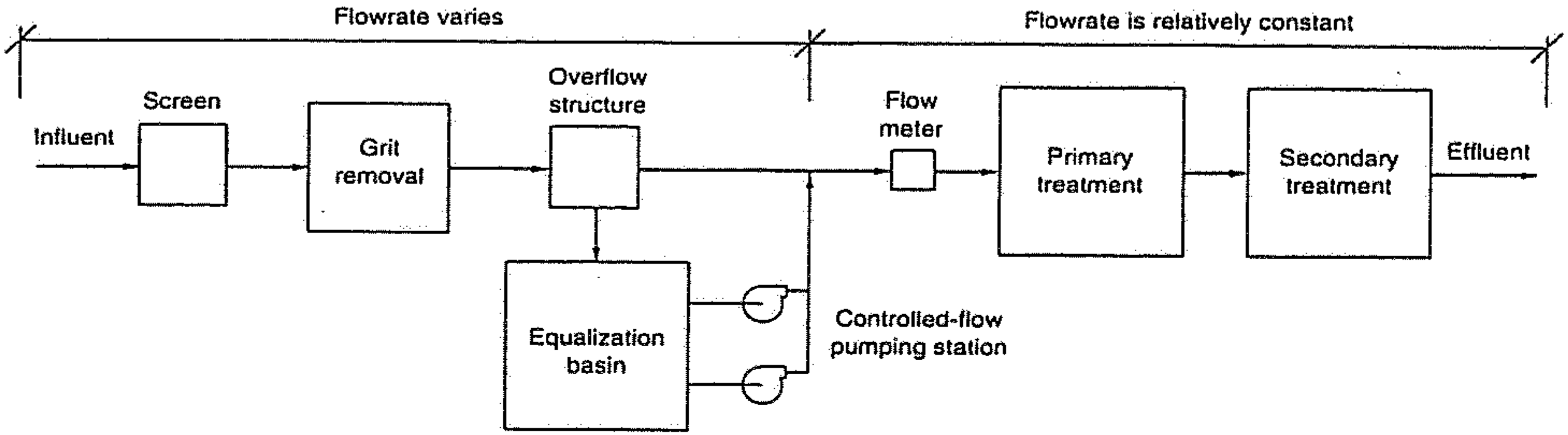
☻ Capital costs increase

Equalisation Tank

In-line Equalisation: **Good Concentration and Flowrate damping**



Off-line Equalisation: **Minimize Pumping Requirements**

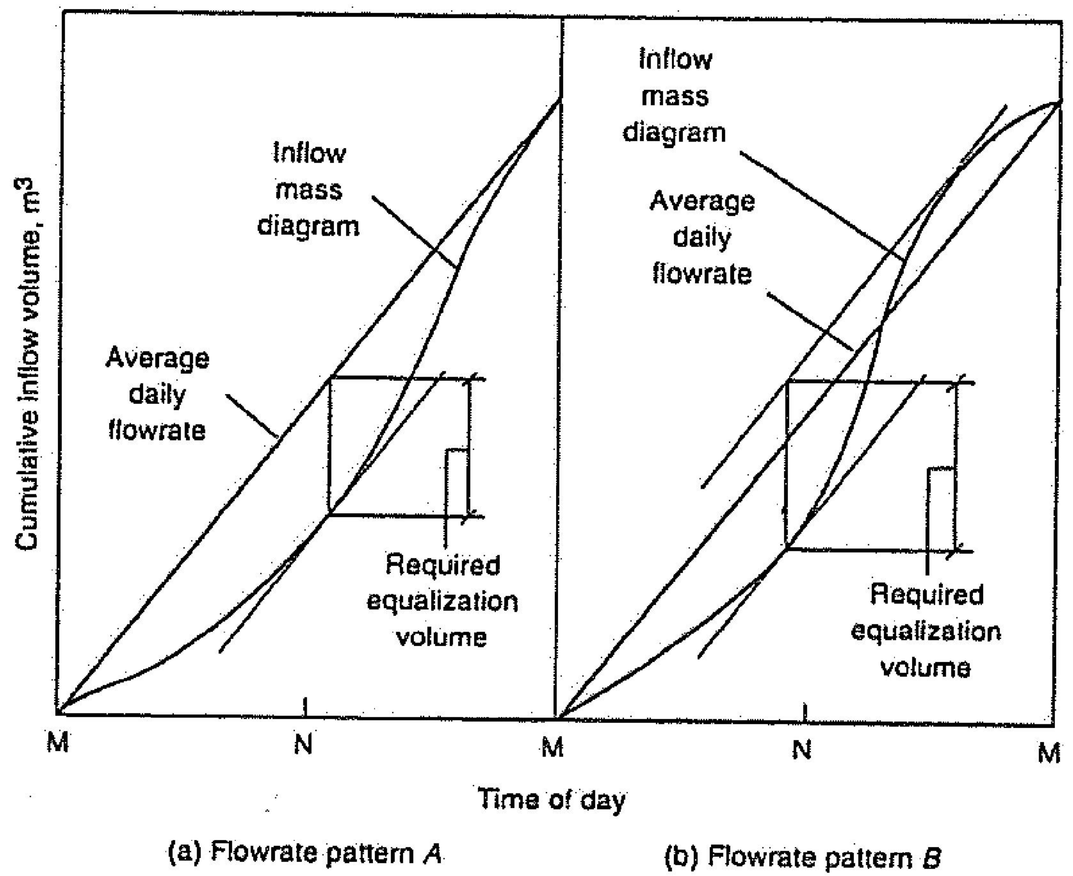


Equalisation Tank

Inflow cumulative volume diagram

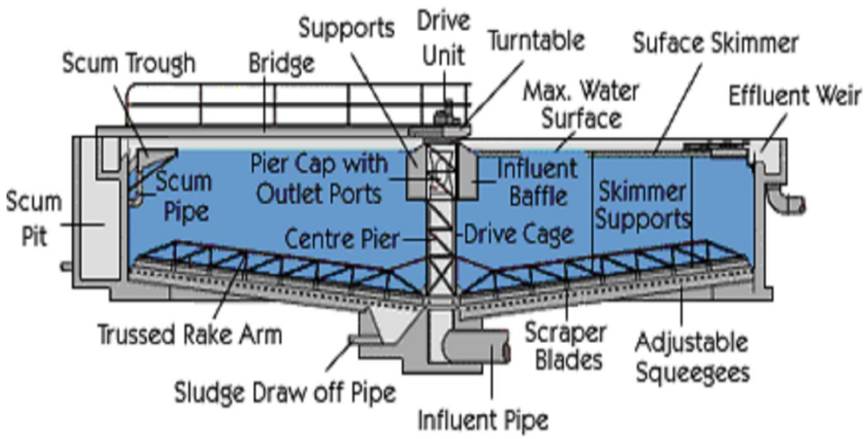
Figure 5-11

Schematic mass diagrams for the determination of the required equalization basin storage volume for two typical flowrate patterns.

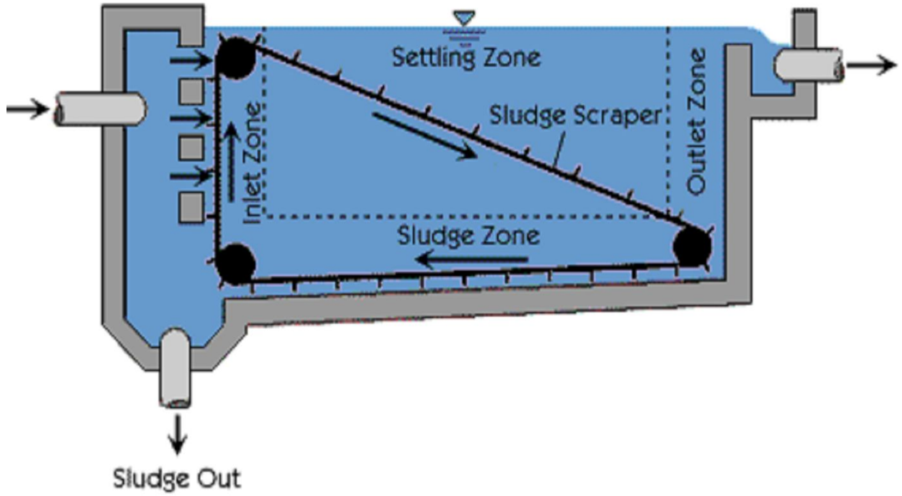


In practice, 10 – 20 % larger than the theoretical one to account for: Internal recycle streams, unforeseen diurnal peaks,

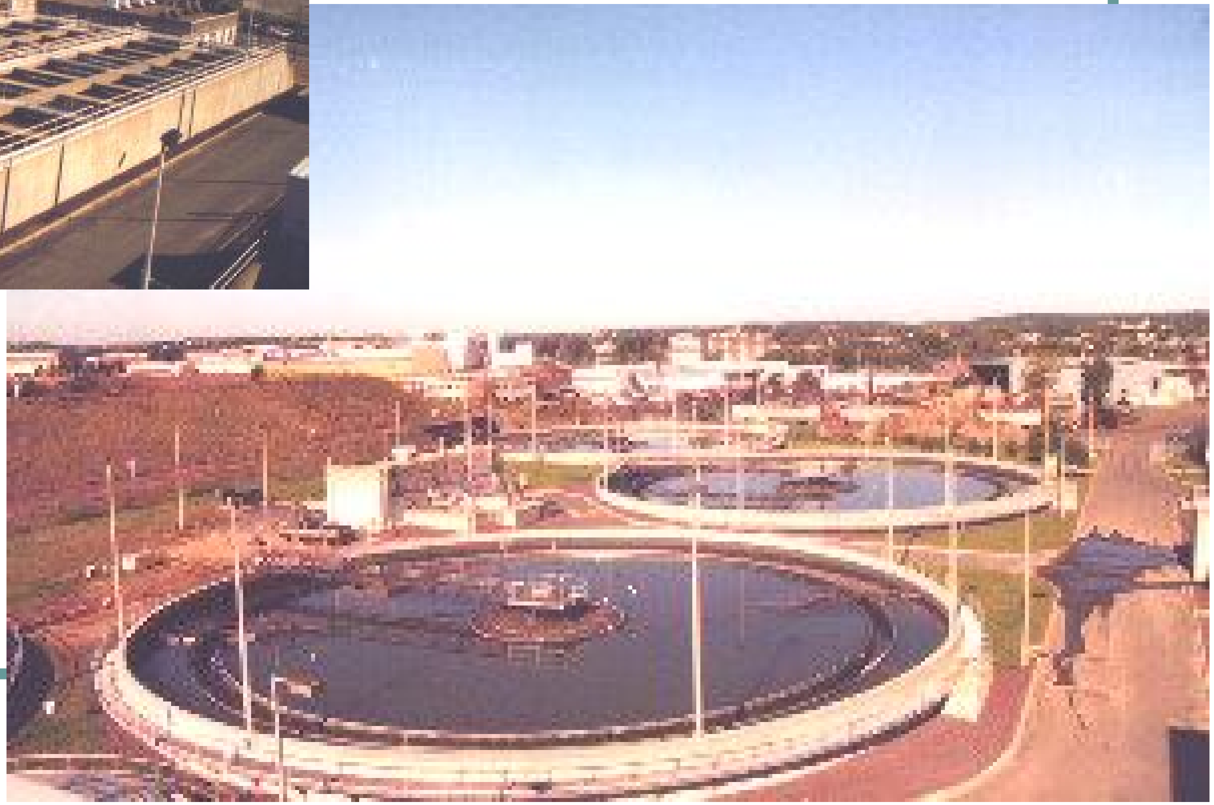
Primary treatment



- Physical separation of solids and greases from the wastewater by sedimentation



Examples



Secondary treatment

- Biological removal of dissolved organic material and/or nutrients
- The most common processes are ponds (small scales), activated sludge systems and trickling filters.
- Generate sludge (VSS) that often needs to be removed

Examples

Tertiary treatment

- Removal of nitrates: Biological Nitrification/Denitrification

  Assimilation into algal biomass

- Removal of phosphates: Coagulation + Flocculation or biological
- Removal of pathogens: UV, chlorine, ozone, ponds
- Special treatment for recalcitrant chemicals: Carbon adsorption, AOPs, air stripping

Sludge handling

Why sludge handling???

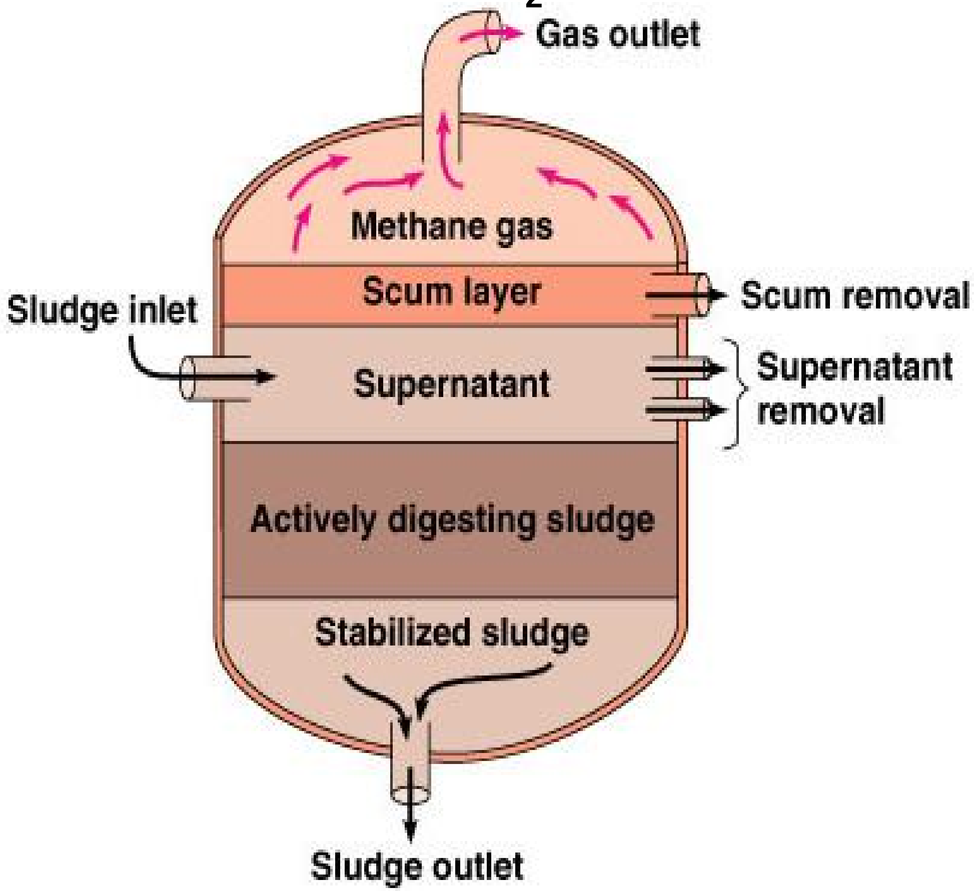
- Reduce pathogens sludge volume & energy production: Aerobic/Anaerobic digestion
- Reduce water content: Thickening/dewatering by sedimentation, drying, centrifugation, press filters
- Final treatment: Incineration or disposal in landfill or composting

Example

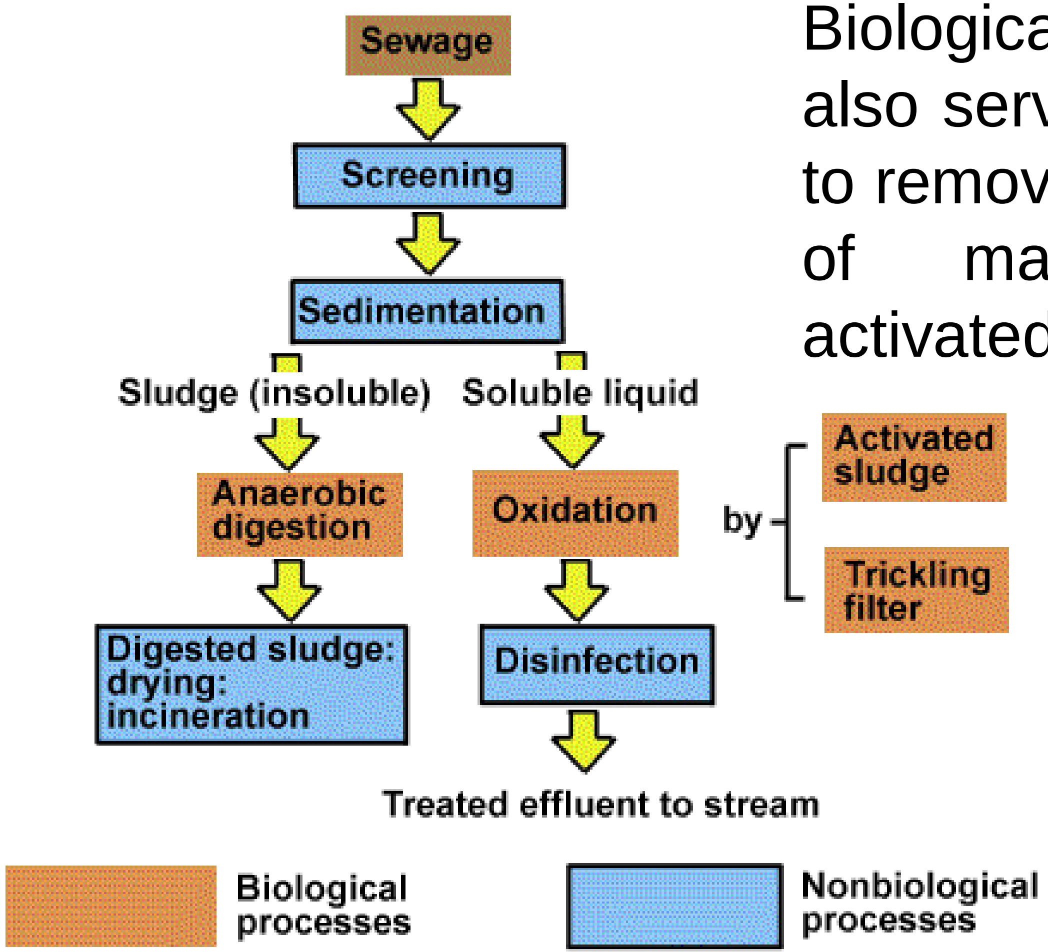
CH_4- 60- 75 %

CO_2: 20-40 %

H_2S: < 2 %



Remember that biological treatment are never alone!!!



Biological processes can also serve for gas treatment to remove odors → Diffusion of malodours in the activated sludge tank

Example 2

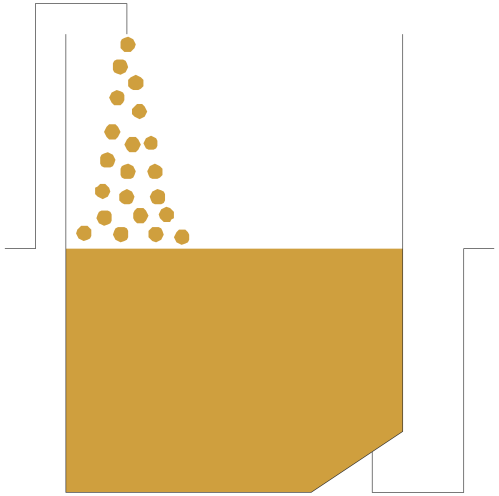
Example 3

Challenges in the WWTP of the 21th Century

- Reduce sludge production
- Remove emerging and persistent organic pollutants
- Improve monitoring
- Upgrade old facilities
- Improve efficiency to meet requirements for water reuse
- Water separation (yellow/grey/brown)
- Reduce energy consumption (approx. 60 % of the total energy cost are due to aeration!!)

In BioWin 3

Equalization Tank: completely mixed vessel in which there is no reaction



Need to specify Volume: → Cumulative volume Diagram Method

Two operation modes:

- Constant Liquid Volume in the Tank (Inflow rate = Outflow rate) → Concentration Damping
- Variable Liquid Volume in the Tank (Need to specify the **Outflow rate** and **Initial liquid hold-up**)→ Flow rate and Concentration Damping

Assignment: Equalization Tank Design and Simulation in BioWin 3