Anaerobic processes
Toxic & recalcitrant organic compound removal

Anaerobic fermentation & oxidation

- **Applications**
  - Treatment of waste sludge & high-strength organic wastes
  - Pretreatment step for conventional biological treatment

- **Advantage**
  - Low biomass yield
  - Energy production in the form of methane (of recent interest!)
    - WWTP -- ~3% of total energy cost in USA
    - Target on energy positive treatment of wastewater

- **Disadvantage**
  - Effluent quality usually not as good as aerobic treatment

Anaerobic fermentation & oxidation

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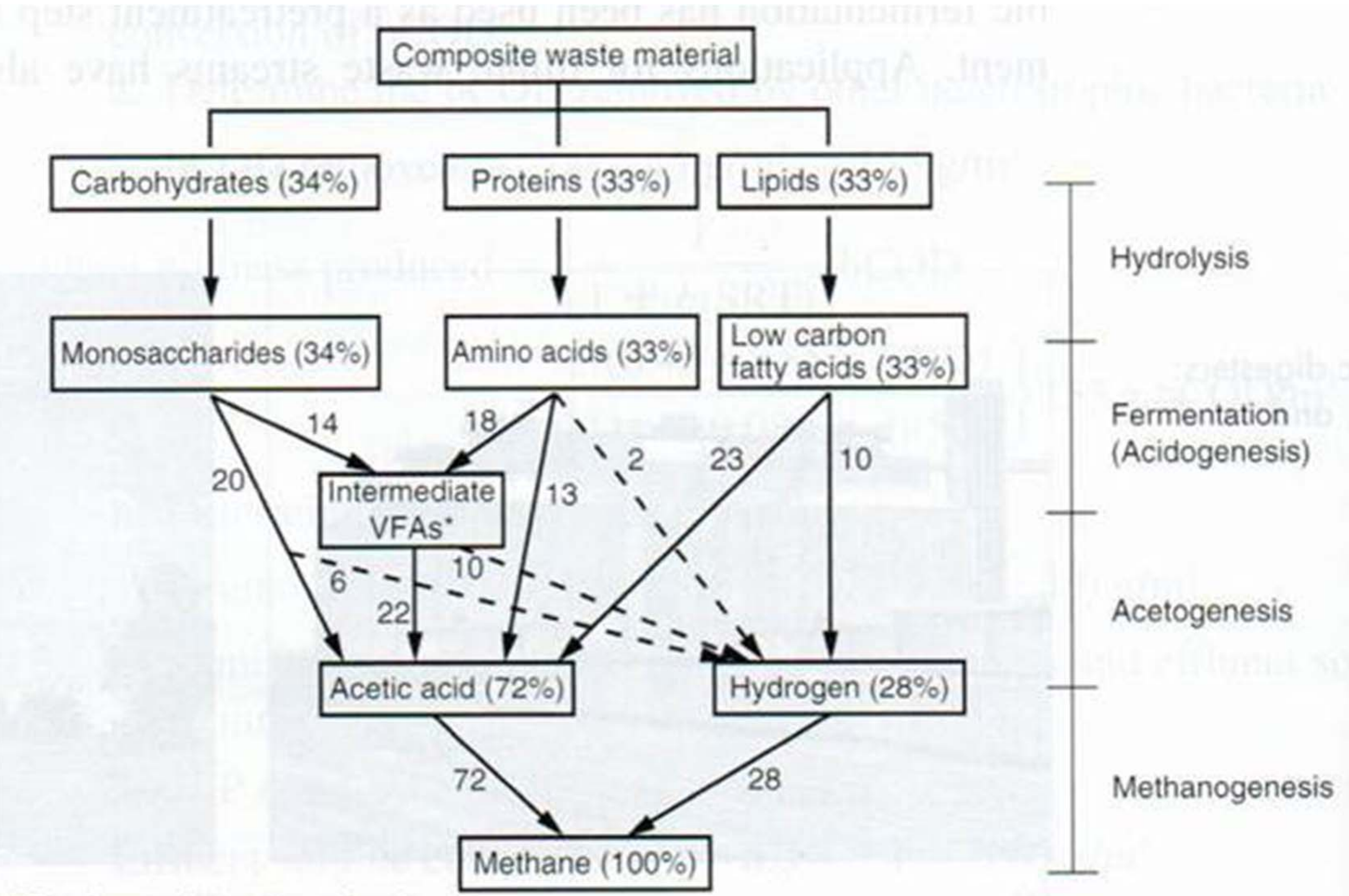
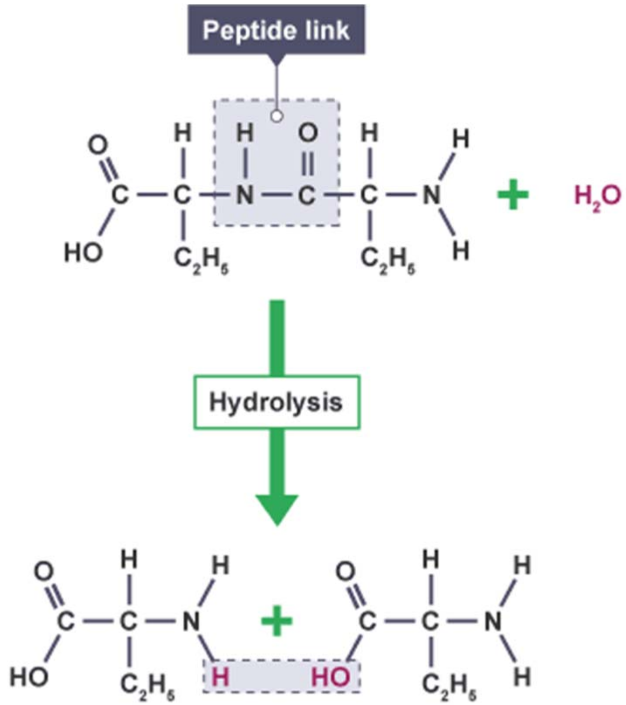


* Propionate, butyrate, valerate

Anaerobic fermentation & oxidation

- **Hydrolysis**
  - Particulates - - - -→ Soluble molecules - - - -→ Monomers
  - By extracellular enzymes
- **Acidogenesis (fermentation)**
  - Use: sugars, amino acids, fatty acids (both e- donor & acceptor)
  - Produce: VFAs, CO_2, H_2
- **Acetogenesis**
  - Use: VFAs other than acetate
  - Produce: acetate, H_2, CO_2



Anaerobic fermentation & oxidation

- **Methanogenesis**
  - By methanogens (belongs to domain **Archaea**)
  - Two groups of methanogens
    - *aceticlastic* methanogens: acetate → $CH_4 + CO_2$
    - *hydrogenotrophic* methanogens: $H_2 + CO_2$ → CH_4
  - In anaerobic digestion process, ~72% methane from acetic acid & ~28% from H_2 (→ gas production of ~65% CH_4 & ~35% CO_2)

- **Syntrophic relationship**
  - Methanogens – acidogens & acetogens
    - Acidogens & acetogens: produce H_2, acetate, etc.
    - Methanogens: cleans up the acido/acetogenesis end products
  - *"Interspecies hydrogen transfer"*

COD balance for anaerobic process

(COD utilized) = (Biomass COD) + (Methane COD)

- No e^- acceptor consumed!
- COD of methane = 2.86 g COD/L CH_4 (@ 0°C, 1 atm)

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Anaerobic fermentation & oxidation

Q: An anaerobic reactor, operated at 35°C, is used to process a wastewater stream with a flow of 3000 m^3/d and a bCOD concentration of 5000 g/m^3. At 95% bCOD removal and a net biomass yield of 0.04 g VSS/g COD, what is the amount of methane produced in m^3/d?

Process kinetics

- Low yield coefficients
  - Low energy gain by chemical transformation
  - Fermentation: Y ~ 0.06 g VSS/g COD; b ~ 0.02 d^{-1}
  - Methanogenesis: Y ~ 0.03 g VSS/g COD; b ~ 0.008 d^{-1}

- Consider two steps:
  - Hydrolysis
  - Soluble substrate utilization for fermentation and methanogenesis
    - Methanogenesis the rate-limiting step

- High SRT is needed (around 40 d) due to slow degradation rate

Process stability

- Kinetics of VFA production is faster than utilization (methanogenesis)
- At steady state, sufficient methanogen population is established to maintain low VFA concentration (<200 g/m^3) & pH≥7.0
- Unstable digester operation may develop under transient loading conditions (VFA production > utilization): VFA accumulation & pH drop
- Low pH leads to decline in methanogenic activity: process failure
- Methanogenic inhibition can also occur by acetate accumulation (acetate conc. > 3000 g/m^3)

Toxic & recalcitrant organic cmpd removal

- **Xenobiotic compounds: man-made**
  - Many are resistant to biodegradation and have potential toxicity to ecosystem & human health
- **Refractory, recalcitrant – not easily biodegradable**
- Some <u>specific</u> microorganisms may have the ability to degrade toxic and recalcitrant compounds

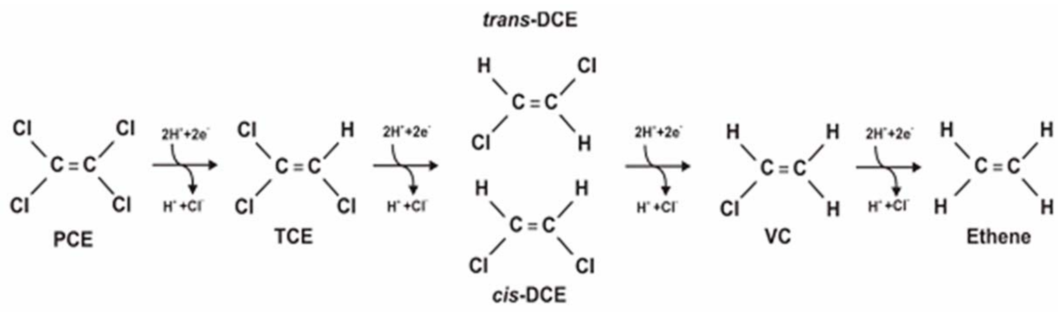
Examples of toxic & recalcitrant organics

Type of waste	Types of organic compounds
Petroleum	alkanes; alkenes; polyaromatic hydrocarbons; monocyclic aromatics – benzene, toluene, ethylbenzene, xylenes; naphthenes
Non-halogenated solvents	alcohols; ketones; esters; ethers; aromatic and aliphatic hydrocarbons; glycols; amines
Halogenated solvents	chlorinated methanes – methylene chloride, chloroform, carbon tetrachloride; chlorinated ethenes – tetrachloroethene, trichloroethene; chlorinated ethanes – trichloroethane; chlorinated benzenes
Insecticides, herbicides, fungicides	organochloride compounds; organophosphate compounds; carbamate esters; phenyl ethers; creosotes; chlorinated phenols
Munitions and explosives	nitroaromatics – trinitrotoluene; nitramines; nitrate esters
Industrial intermediates	phthalate esters; benzene; phenol; chlorobenzenes; chlorophenols; xylenes
Transformer and hydraulic fluids	polychlorinated biphenyls
Production byproducts	dioxin, furans

Biodegradation pathways

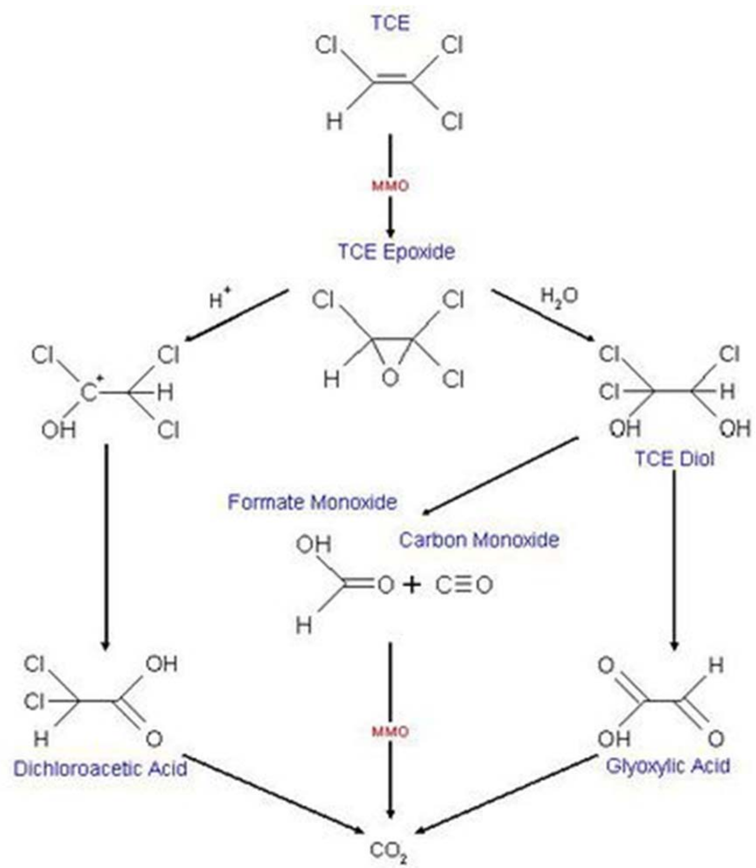
- **Compound serving as a growth substrate**
  - Complete mineralization or transformation to a different compound (hopefully less or non-toxic)
  - Aerobic degradation usually more significant than anaerobic
  - Aerobic degradation works for many non-halogenated organic compounds, but not often for halogenated compounds

- **Compound as an e^- acceptor**
  - Reductive dechlorination
    - Under anaerobic condition
    - Uses H_2 as an e^- donor – substitution of Cl with H in the organic molecule
    - PCE, TCE, PCP, etc.



Biodegradation pathways

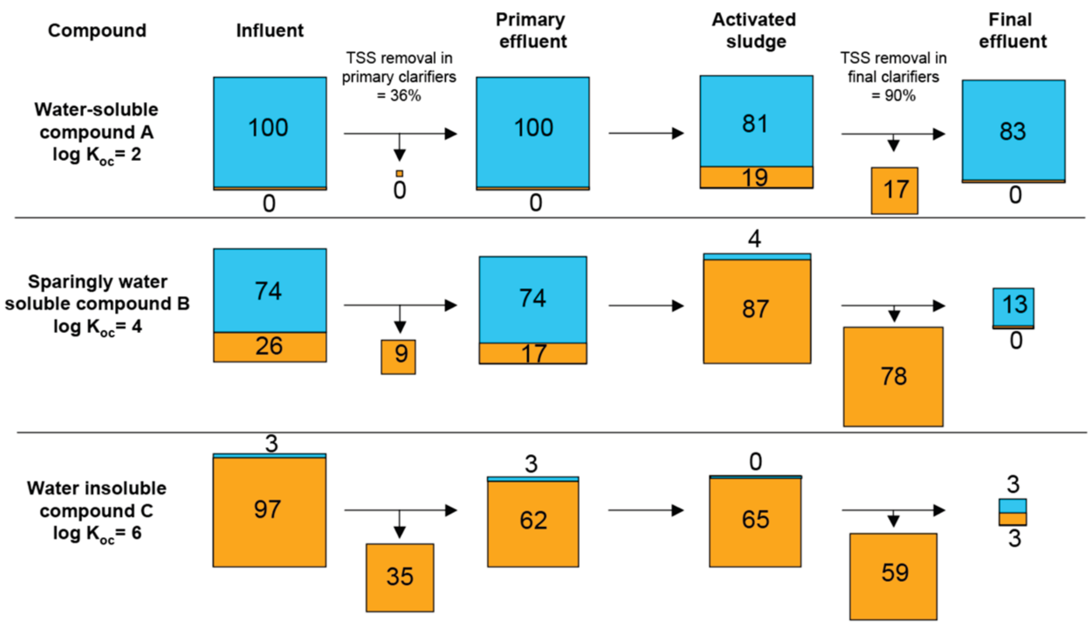
- **Cometabolism**
  - Degradation pathway for chlorinated organic compounds under aerobic condition
  - By bacteria producing nonspecific mono-oxygenase or dioxygenase enzymes
  - Example organisms: methanotrophic bacteria, phenol/toluene oxidizers



http://microbewiki.kenyon.edu

Abiotic losses

- May be significant for many toxic & recalcitrant compounds
- Adsorption to biomass in secondary treatment
  - Removed from wastewater as sludge
  - Issues with sludge application and disposal
- Volatilization: released to the atmosphere



Fate of non-biodegradable and non-volatile organic compounds during conventional wastewater treatment

Heidler & Halden (2008) ES&T 42:6324-6332.