Toxic and recalcitrant compound removal

Toxic & recalcitrant organic compounds

- The pollutants we have focused on so far are:
  - those that result in gross impact on aquatic environment/ecosystem
    - oxygen-demanding materials: DO / N & P containing materials: eutrophication
    - no specific toxicity
  - biodegradables

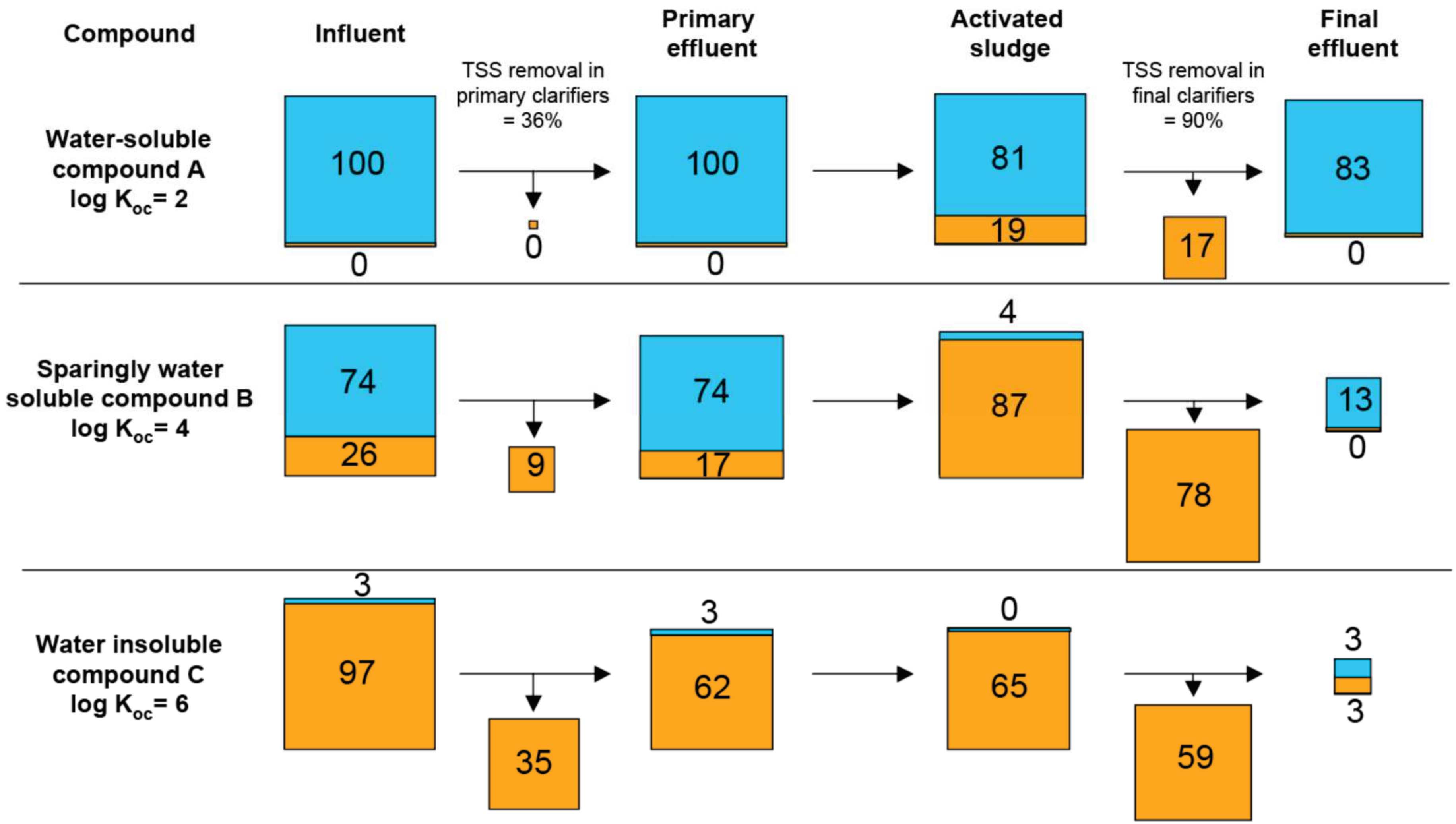
- **Xenobiotic compounds: man-made**
  - Many are resistant to biodegradation and have potential toxicity to ecosystem & human health
- **Refractory, recalcitrant – not easily biodegradable**
- Some <u>specific</u> microorganisms may have the ability to degrade toxic and recalcitrant compounds

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

Abiotic losses in WWTP

- May be significant for recalcitrant compounds
- Adsorption to solids in primary/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

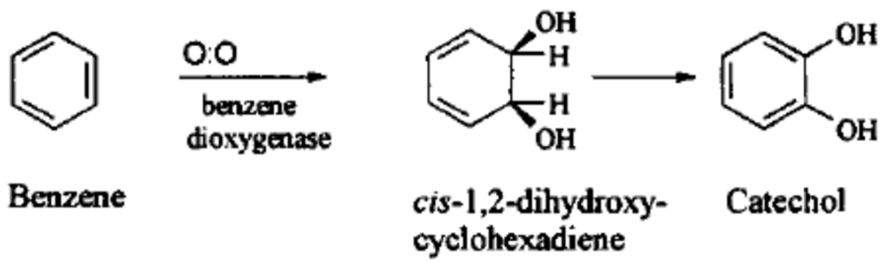
Heidler & Halden (2008) ES&T 42:6324-6332.

Biodegradation pathways (1)

- **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

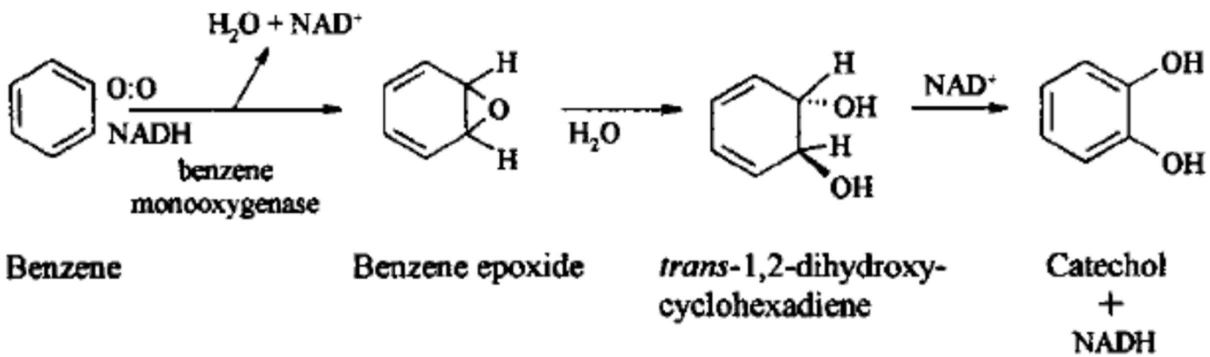
Aerobic biodegradation of aromatics

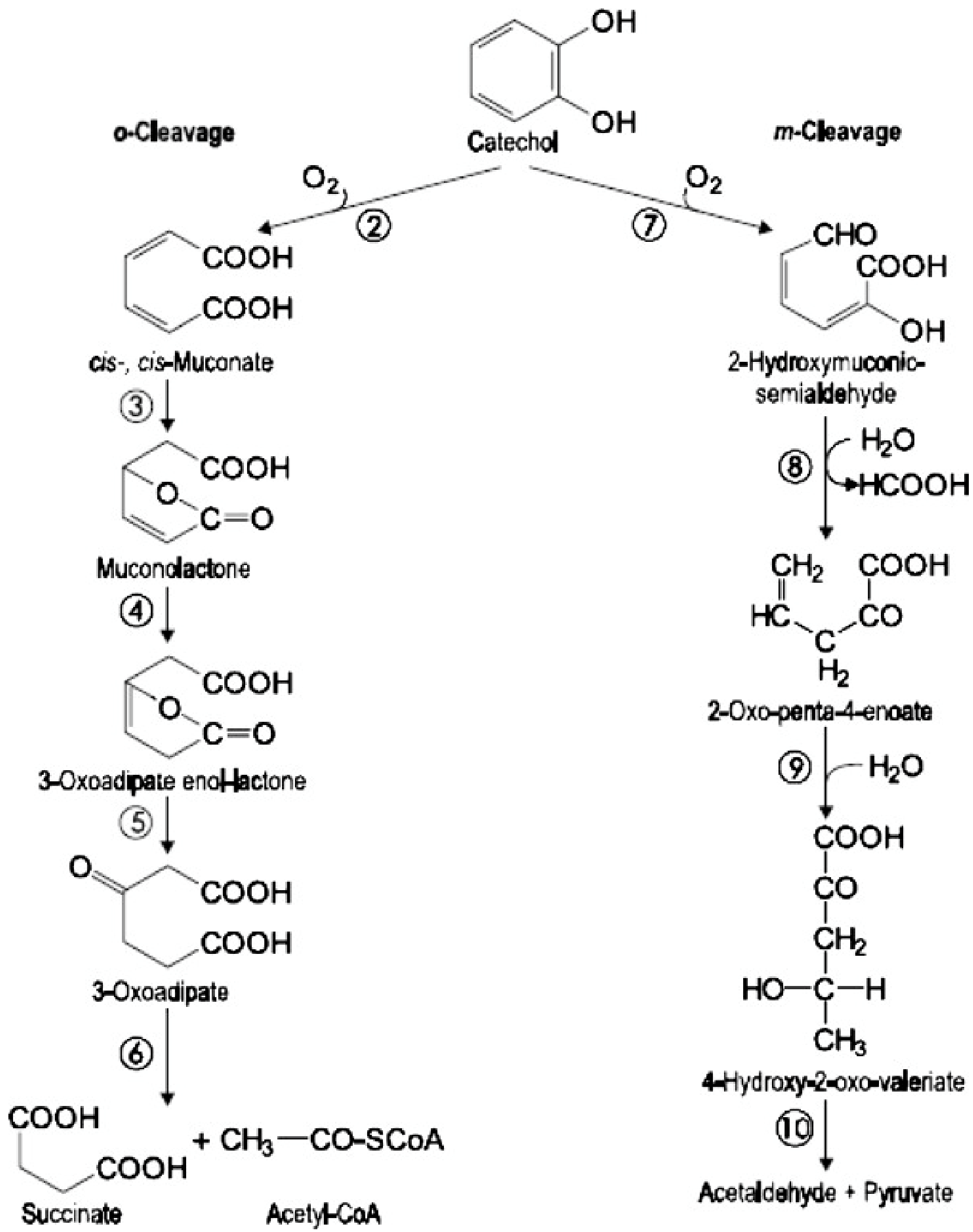
- Aromatic rings are relatively stable
  - Ring cleavage is often the major challenge
- Some specific enzymes are able to insert oxygen into the aromatic ring to initiate the degradation



Proposed aerobic benzene degradation pathways to form a key reaction intermediate, ***catechol***

(Mancini et al., 2003,AEM)

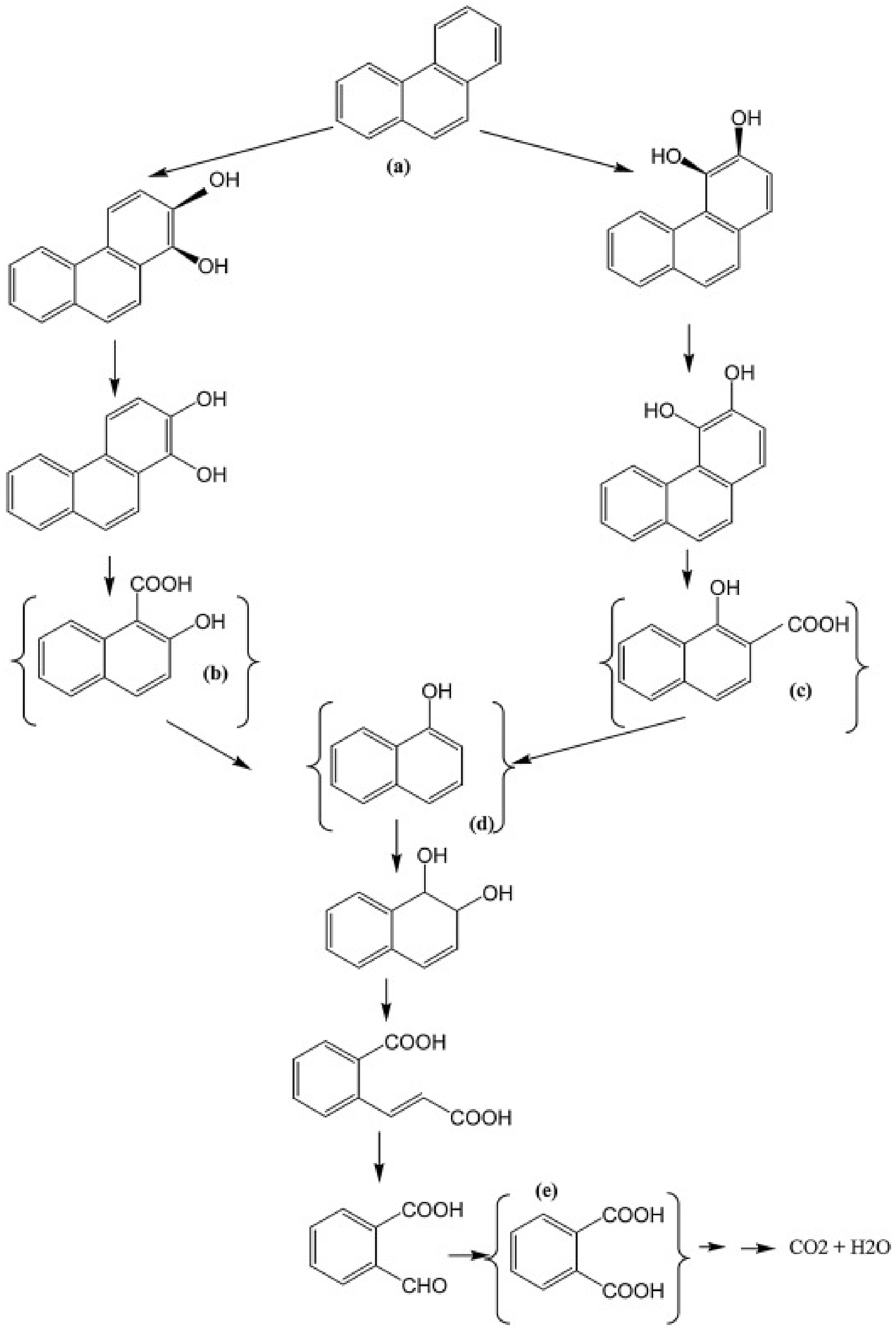




- Catechol degradation is relatively easier

ortho and meta cleavage pathways in aerobic degradation of catechol

(ref: Environmental Biotechnology Concepts and Applications)

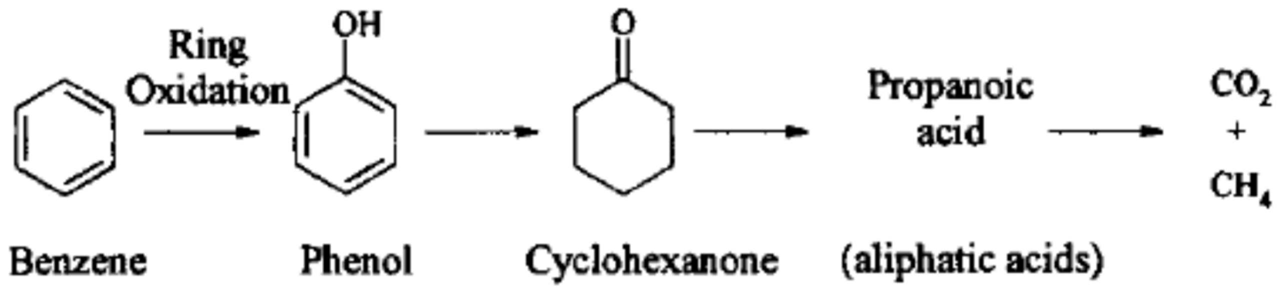


- Similar pathway applies for some other aromatics (e.g., polycyclic aromatic hydrocarbons, PAHs)

Proposed aerobic biodegradation pathway of phenanthrene by consortium PHMM

(Mnif et al., 2017, Health Advance)

Anaerobic biodegradation of aromatics



Proposed anaerobic benzene degradation pathway *(Mancini et al., 2003,AEM)*

- May involve pathways & enzymes different from aerobic biodegradation

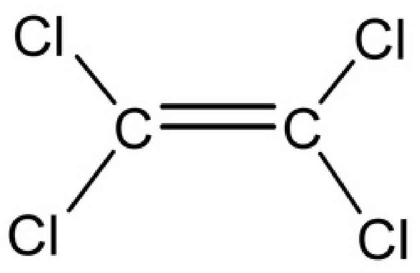
Biodegradation pathways (2)

- **Compound as an e^- acceptor**

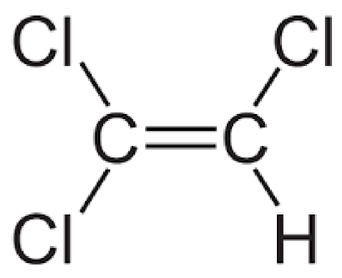
[reductive dehalogenation]

  - Under sulfidogenic/methanogenic condition (highly reduced condition)
  - Uses H_2 as an e^- donor: substitution of a halogen (Cl, F, ..) with H in the organic molecule
  - Reductive dechlorination extensively studied
    - PCE, TCE, PCP, PCBs, etc.

PCE, TCE, PCP, PCBs – typical chlorinated organic pollutants

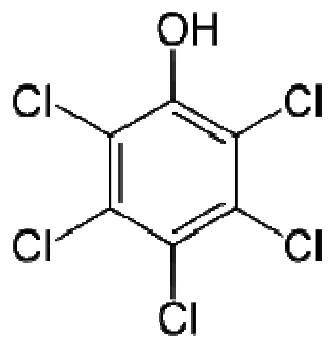


perchloroethylene, PCE
(or tetrachloroethylene)



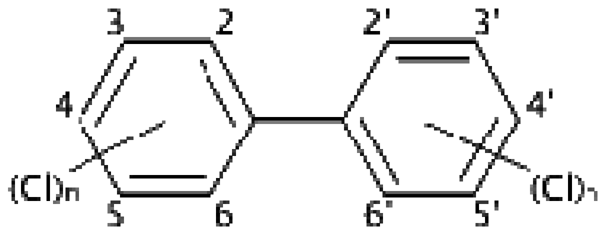
trichloroethylene, TCE

- PCE & TCE: widely used organic solvents (e.g., dry cleaning)



pentachlorophenol, PCP

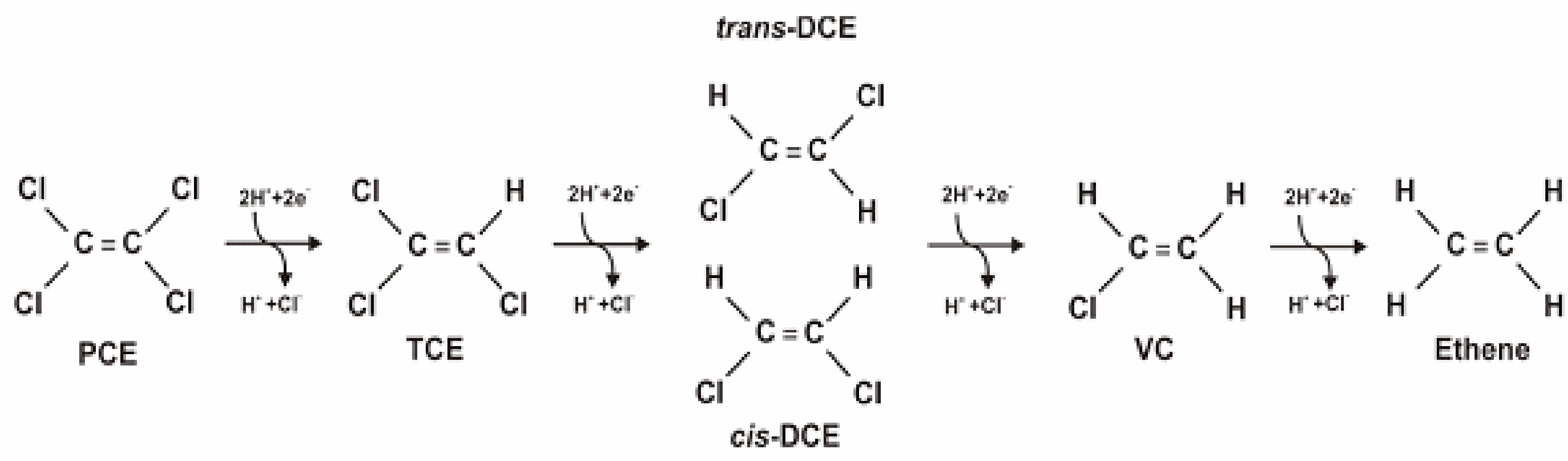
- PCP: pesticide, disinfectant, etc. (e.g., wood preservative)



polychlorinated biphenyls, PCBs

- PCBs: insulator, plasticizer, flame retardants, etc.

PCE dechlorination pathway

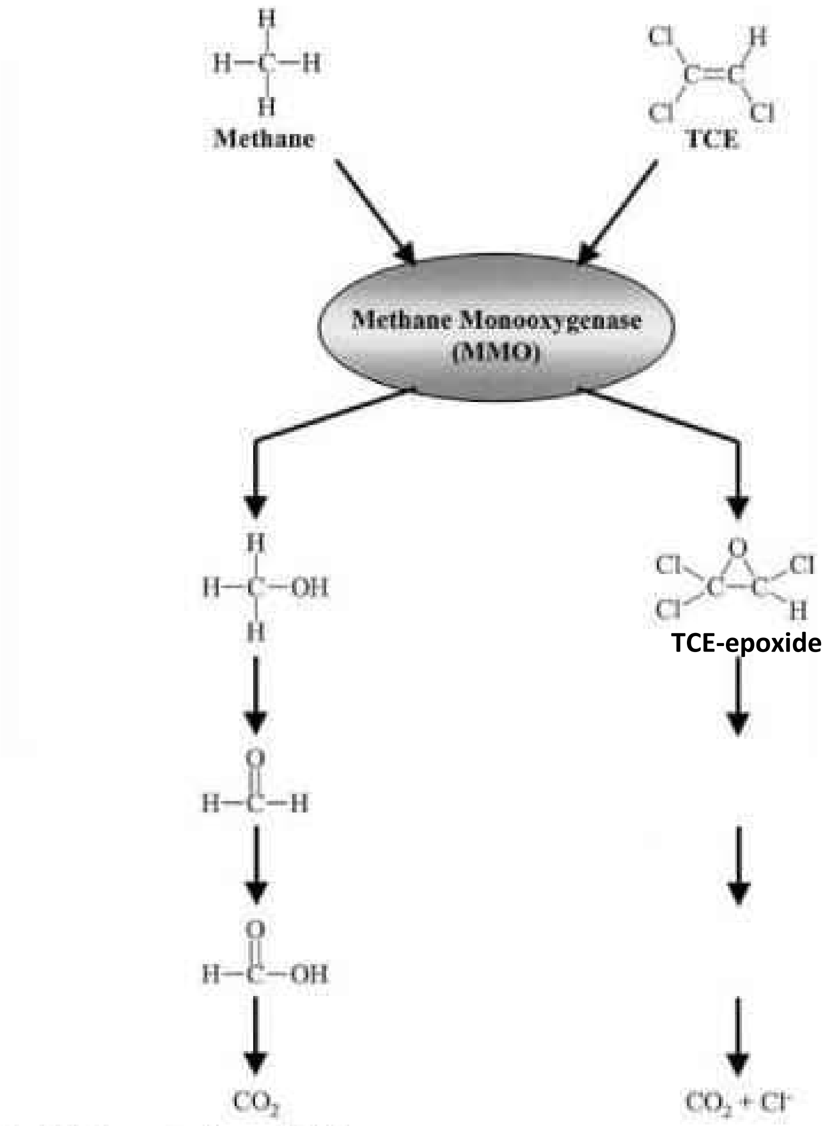


- Ethene can be easily mineralized by other microorganisms
- Dechlorination more challenging for DCE/VC than PCE/TCE
  - Only a very limited number of species can completely reduce PCE to ethene (e.g., *Dehalococcoides ethenogenes*)
  - VC is more toxic than PCE/TCE: possibility of increased toxicity by biotransformation
  - So should confirm that the species capable of complete PCE/TCE reduction to ethene are present at the site for bioremediation

Biodegradation pathways (3)

- **Cometabolism**
  - Transformation of a compound by a microorganism that is unable to use the compound as a carbon or energy source
  - No microorganism growth by 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

Methanotroph transforming TCE by cometabolism



- Methane is a growth substrate
- MMO catalyzes methane oxidation to methanol
- The MMO produced is also capable of catalyzing TCE oxidation to TCE-epoxide
- In pure culture, TCE-epoxide accumulates, but in the environment, it may be further degraded by other microorganisms to be mineralized

Toluene injection for treatment of TCE in GW

Kuo et al., 2004, Water Res.

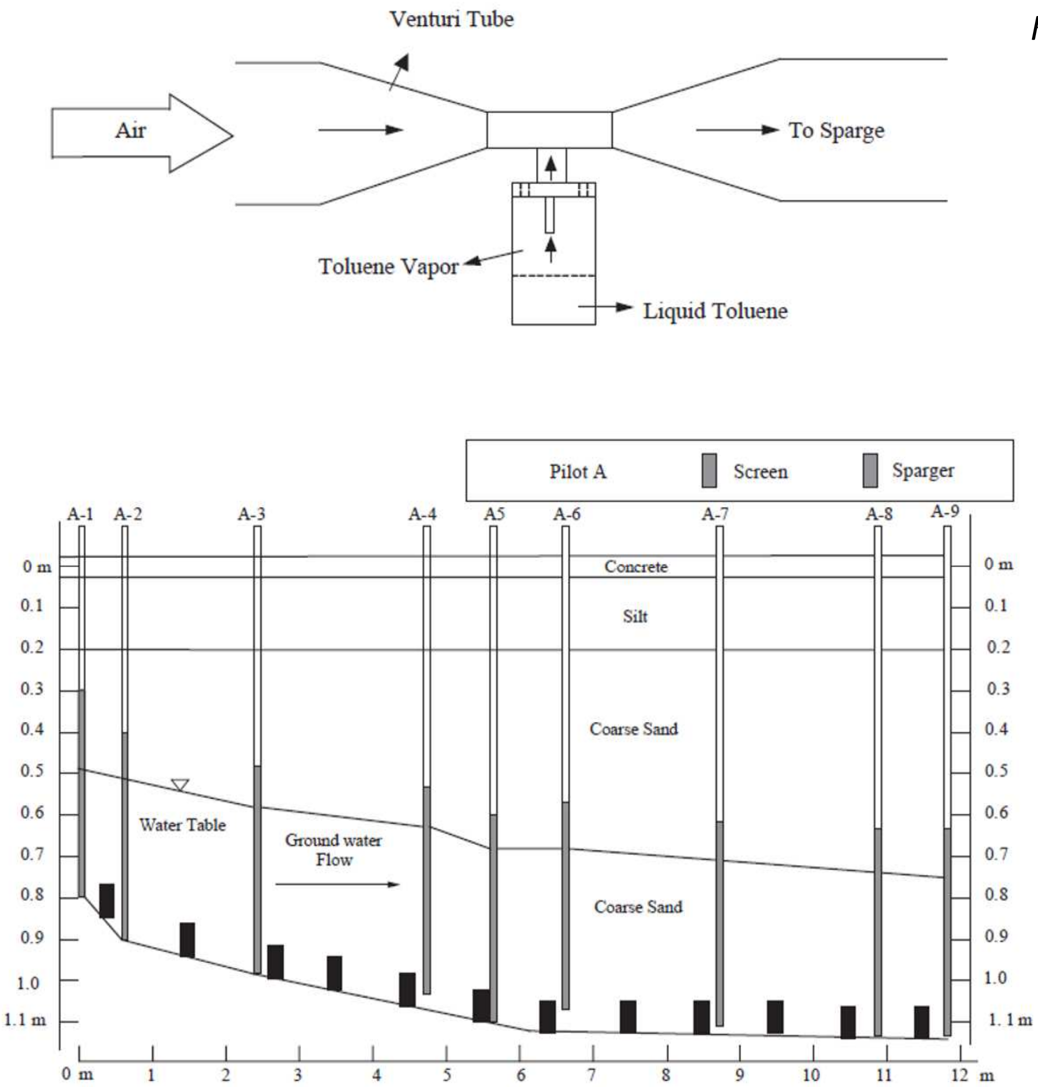


Fig. 1. Schematic diagrams of Pilot A and venturi tube used for toluene-vapor injection.

- Toluene & O_2 injection to promote growth of toluene-oxidizing bacteria
- TCE biodegradation by cometabolism
- >90% TCE removal observed
- Constraint of adding a pollutant to remove another