Recalcitrant compound removal mechanisms

Recalcitrant organic compounds

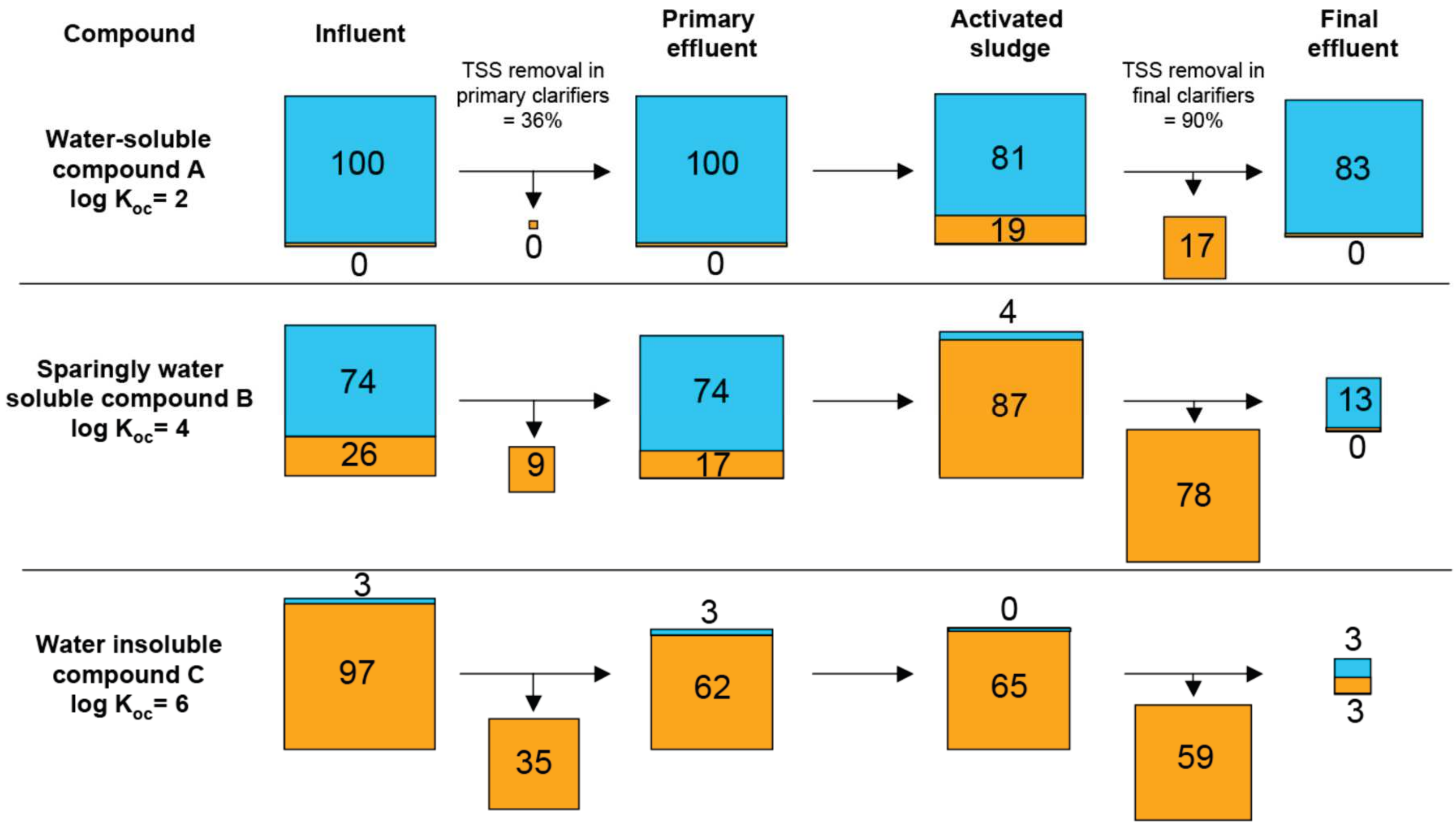
- The pollutants we have focused on so far are:
  - those that result in gross impact on aquatic environment/ecosystem
    - oxygen-demanding materials: DO / N & P containing materials: eutrophication
    - no specific toxicity
  - biodegradables
- In this class, we will consider recalcitrant compounds
- **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 recalcitrant compounds

Examples of toxic and/or 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

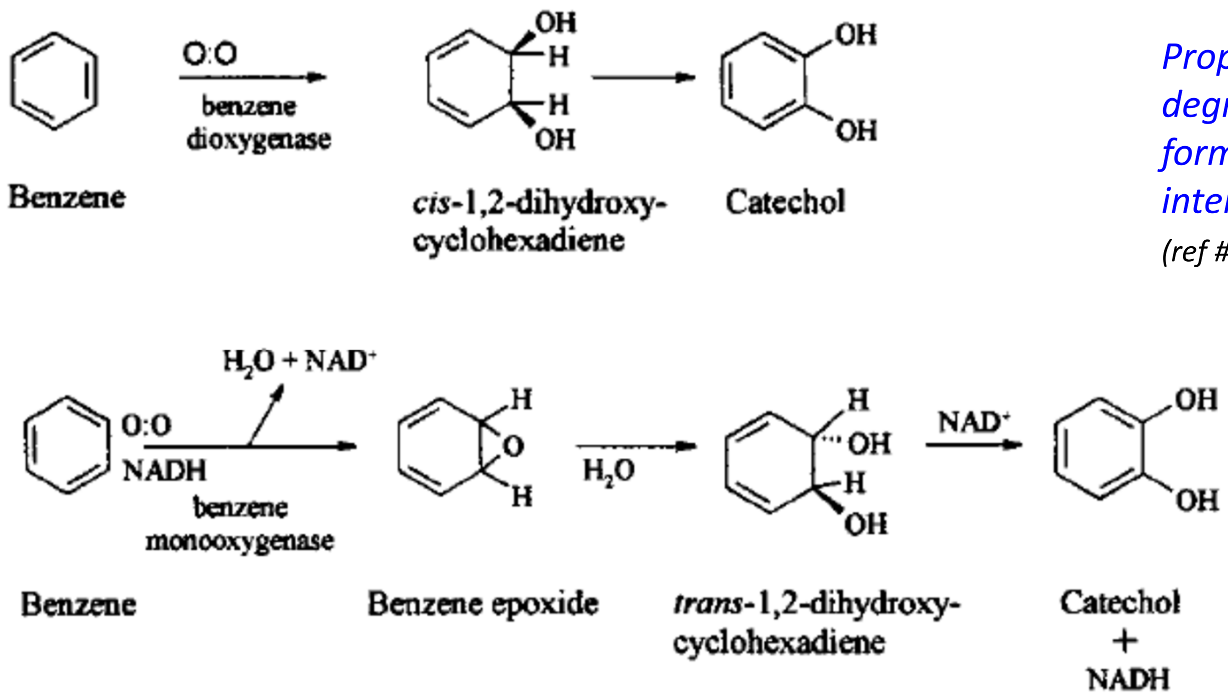
(ref #1)

Biodegradation pathways (1)

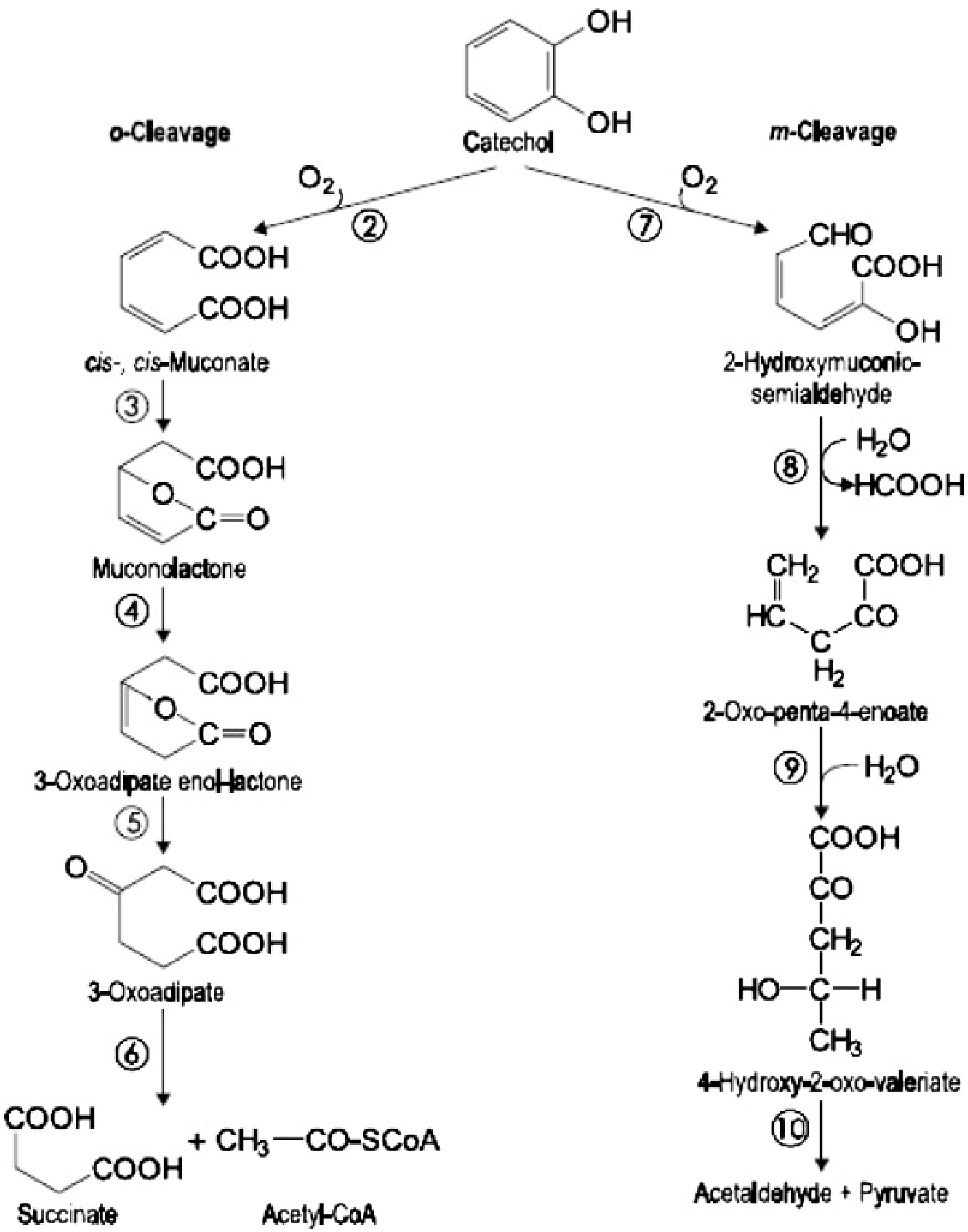
- **Compound serving as a growth substrate**
  - Complete mineralization or transformation to a different compound (hopefully less or non-toxic)
  - Aerobic degradation usually more significant than anaerobic
  - Aerobic degradation works for many non-halogenated organic compounds, but not often for 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*** *(ref #2)*

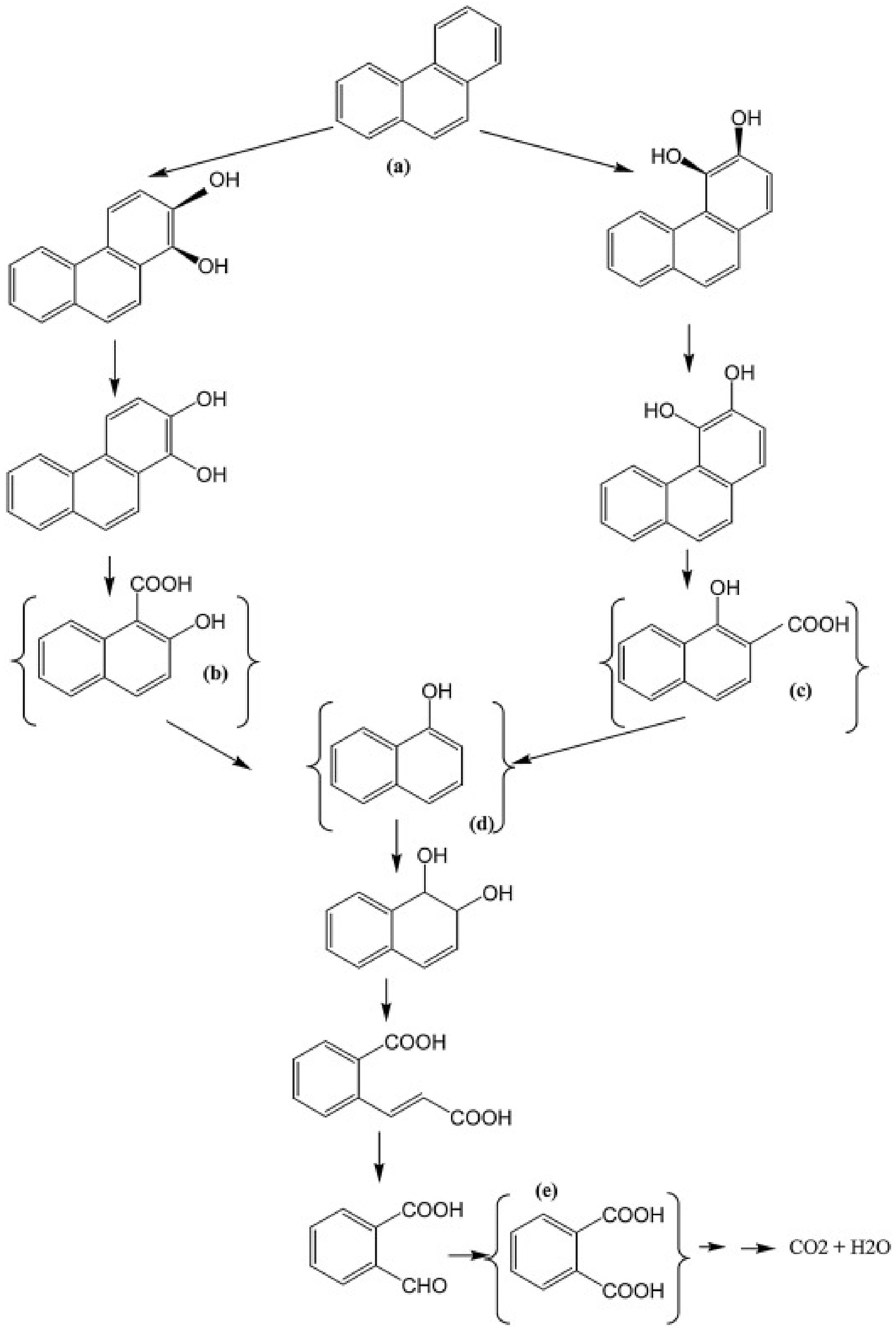


- Catechol degradation is relatively easier

ortho and meta cleavage pathways in aerobic degradation of catechol

(ref #3)

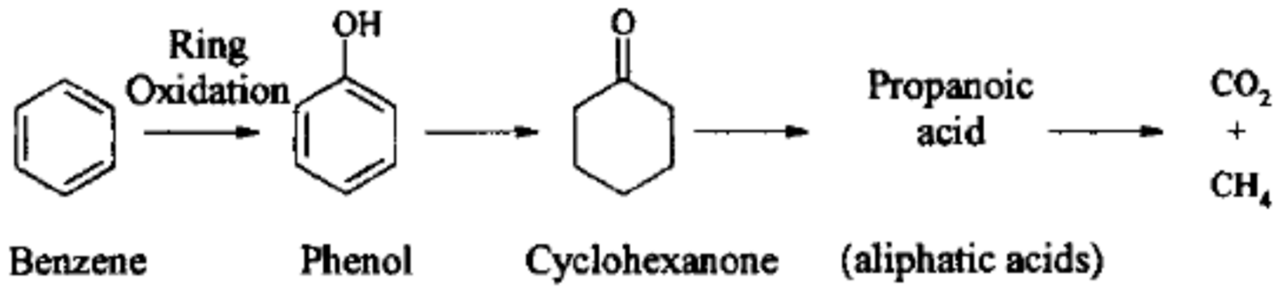
- Similar pathway applies for some other aromatics (e.g., polycyclic aromatic hydrocarbons, PAHs)



Proposed aerobic biodegradation pathway of phenanthrene by consortium PHMM

(ref #4)

Anaerobic biodegradation of aromatics



Proposed anaerobic benzene degradation pathway *(ref #2)*

- May involve pathways & enzymes different from aerobic biodegradation

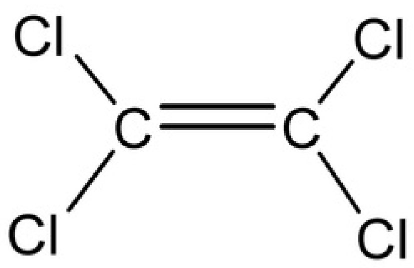
Biodegradation pathways (2)

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

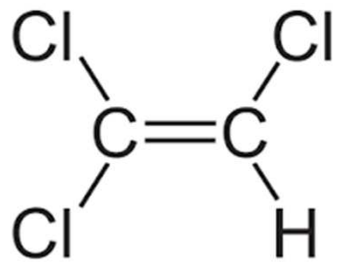
[reductive dehalogenation]

- 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

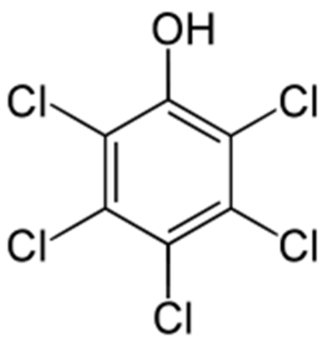


perchloroethylene, PCE
(or tetrachloroethylene)



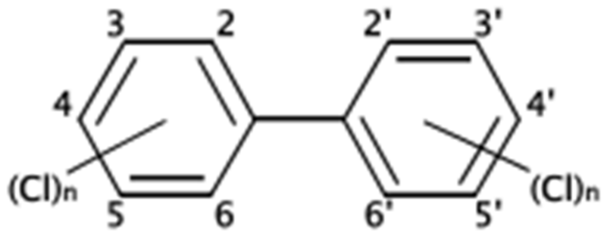
trichloroethylene, TCE

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



pentachlorophenol, PCP

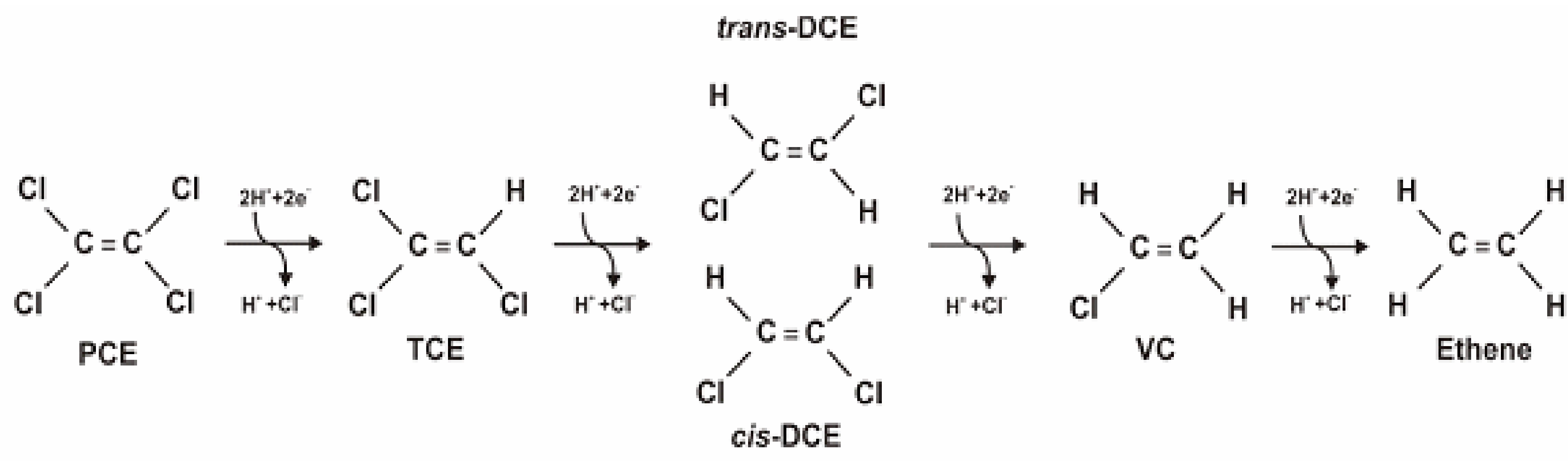
- PCP: pesticide, disinfectant, etc. (e.g., wood preservative)



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 <u>increased toxicity</u> by biotransformation
  - So should confirm that the species capable of complete PCE/TCE reduction to ethene are present at the site for bioremediation

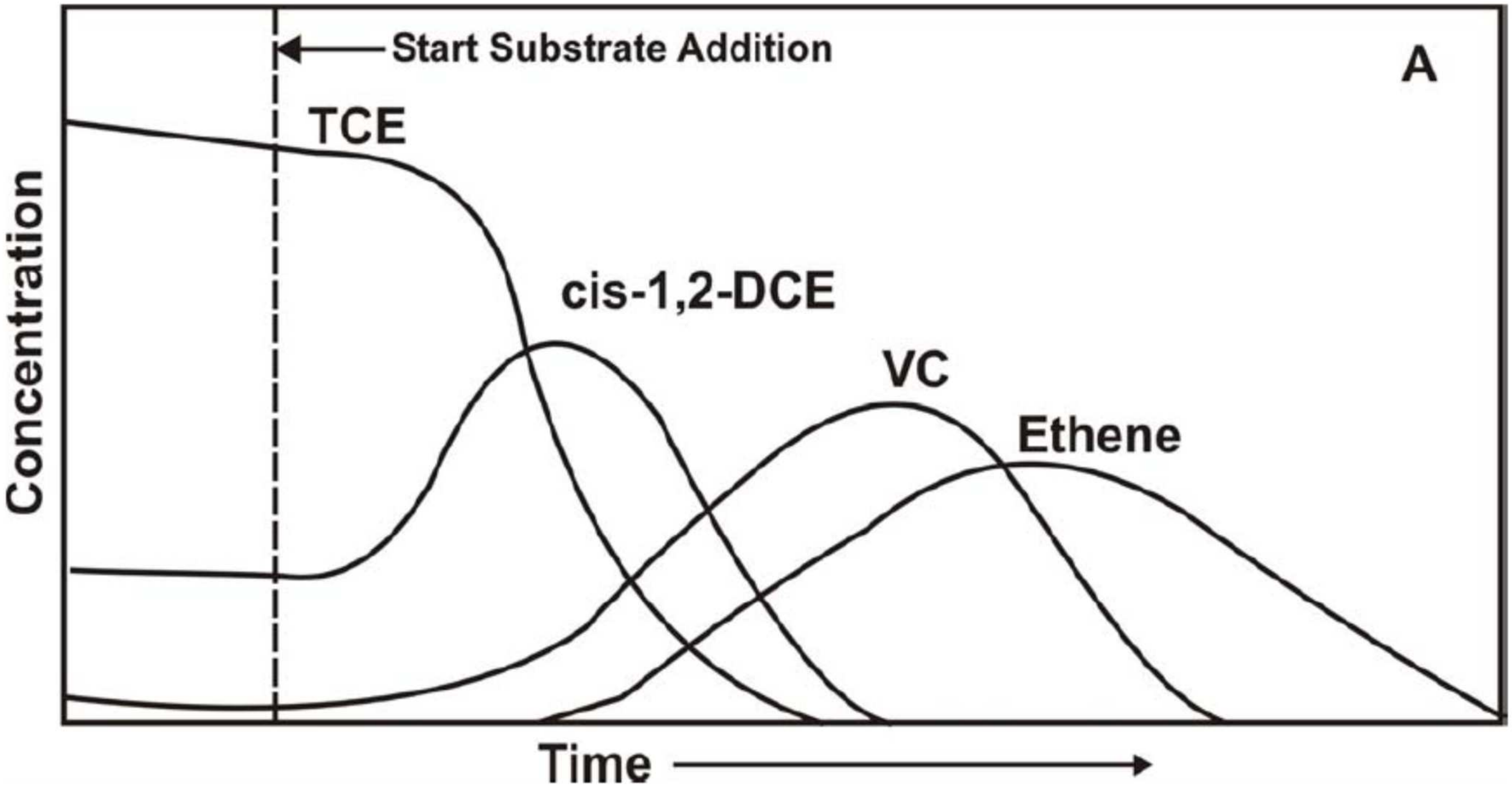


Figure 6.3 Conceptual Changes in Contaminant Molar Concentration over Time with Sequential Anaerobic Dechlorination

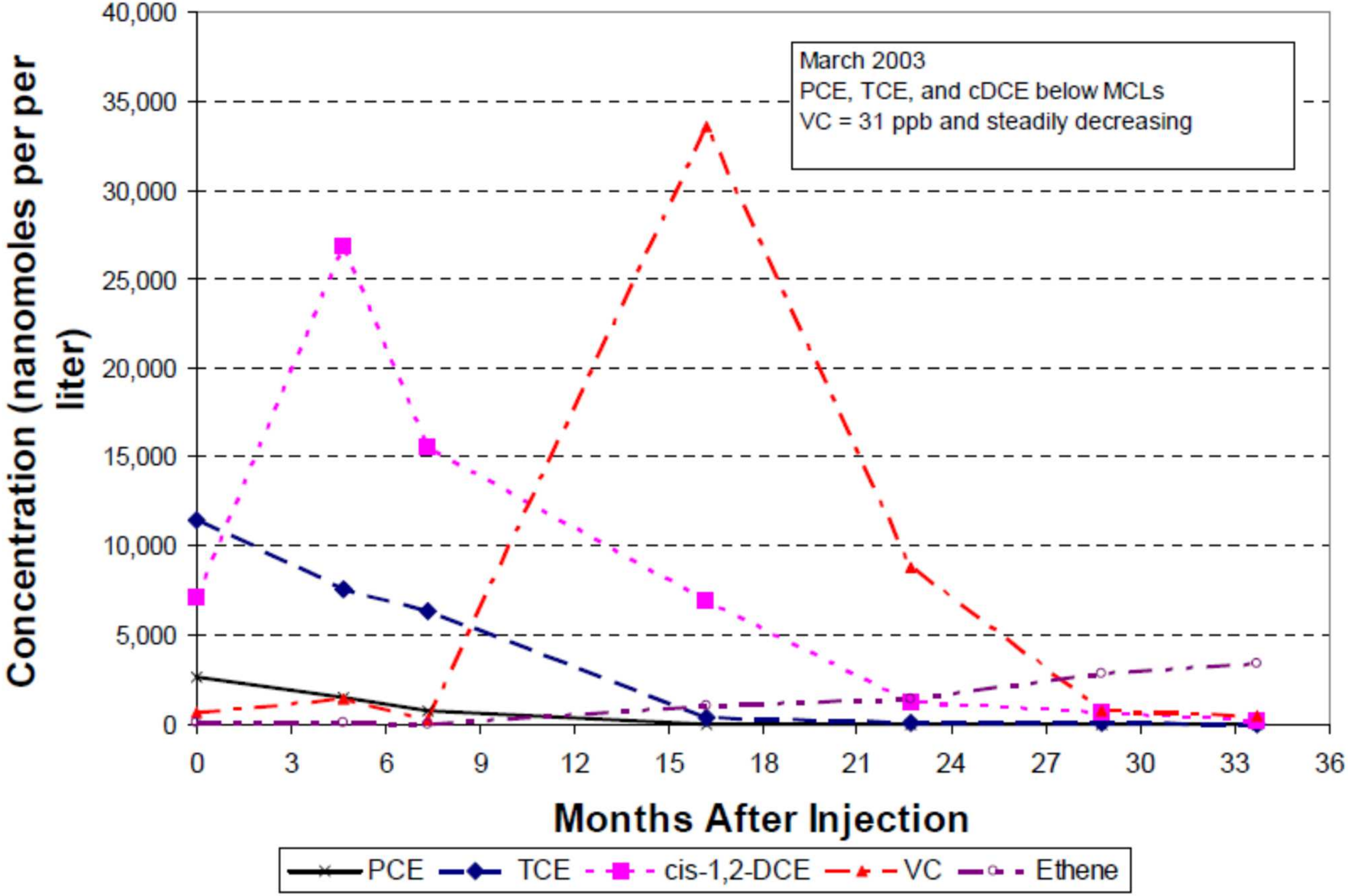
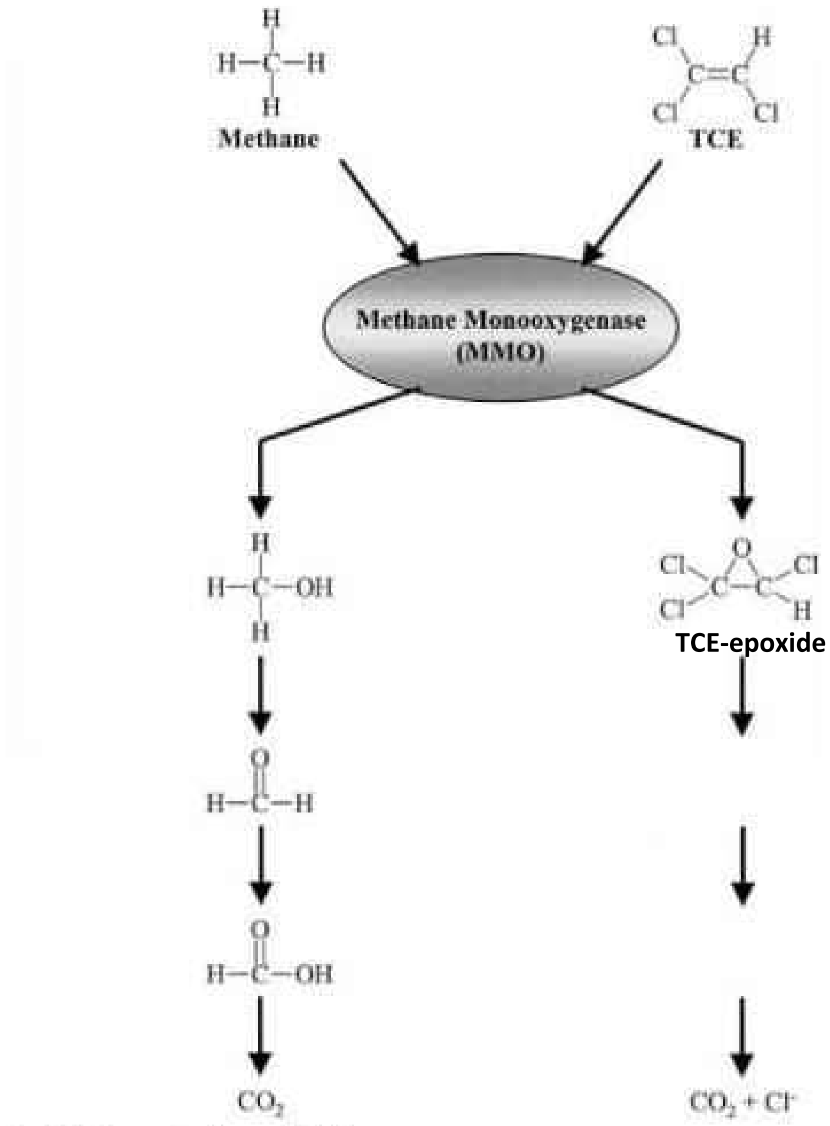


Figure 6.5 Changes in Molar Concentration over Time (Well MW4, Site SS015, Travis AFB, California)

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

(ref #5)

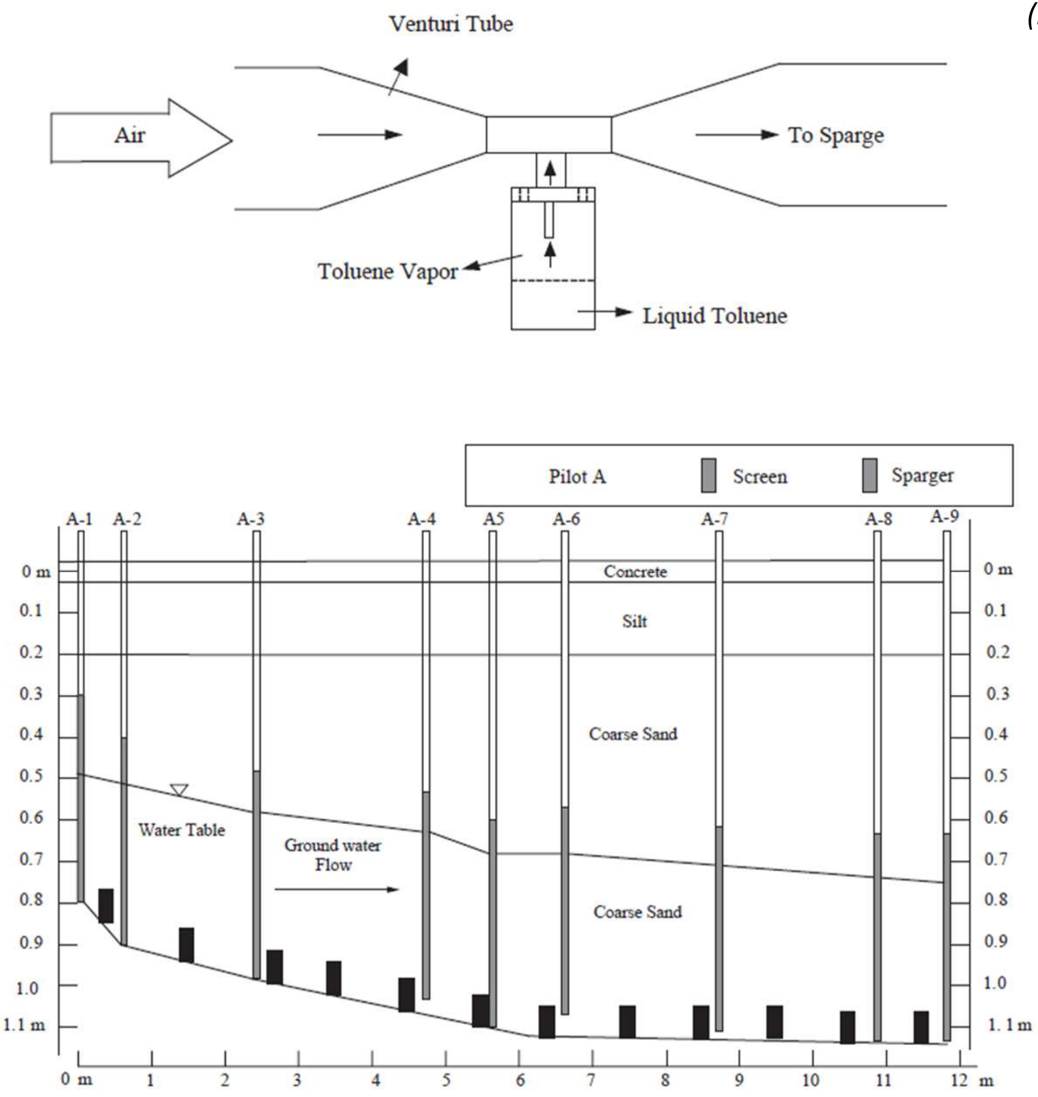


Fig. 1. Schematic diagrams of Pilot A and venturi tube used for toluene-vapor injection.

- 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

References

#1) Heidler, J., Halden, R. U. (2008) Meta-analysis of mass balances examining chemical fate during wastewater treatment. Environmental Science & Technology, 42:6324-6332.

#2) Mancini, S. A., Ulrich, A. C., Lacrampe-Couloume, G., Sleep, B., Edwards, E. A., Lollar, B. S. (2003) Carbon and hydrogen isotope fractionation during anaerobic biodegradation of benzene. Applied and Environmental Microbiology, 69:191-198.

#3) Aghapour, Ali & Moussavi, Gholamreza & Yaghmaeian, Kamyar. (2013) Biological Degradation of Catechol in Wastewater using the Sequencing Continuous-inflow Reactor (SCR). Journal of Environmental Health Science and Engineering. 11. 10.1186/2052-336X-11-3.

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#5) Kuo, M. C. T., Liang, K. F., Han, Y. L., Fan, K. C. (2004) Pilot studies for in-situ aerobic cometabolism of trichloroethylene using toluene-vapor as the primary substrate. Water Research, 38:4125-4134.