Impacts of a Zero Valent Iron PRB on Downgradient Biodegradation Processes

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Why is Downgradient Biodegradation Important?

- Significant contaminant mass and concentration will likely be present in the aquifer downgradient of the PRB for a long time after the PRB is installed
  - Transient processes
  - Steady state processes

Transient Processes

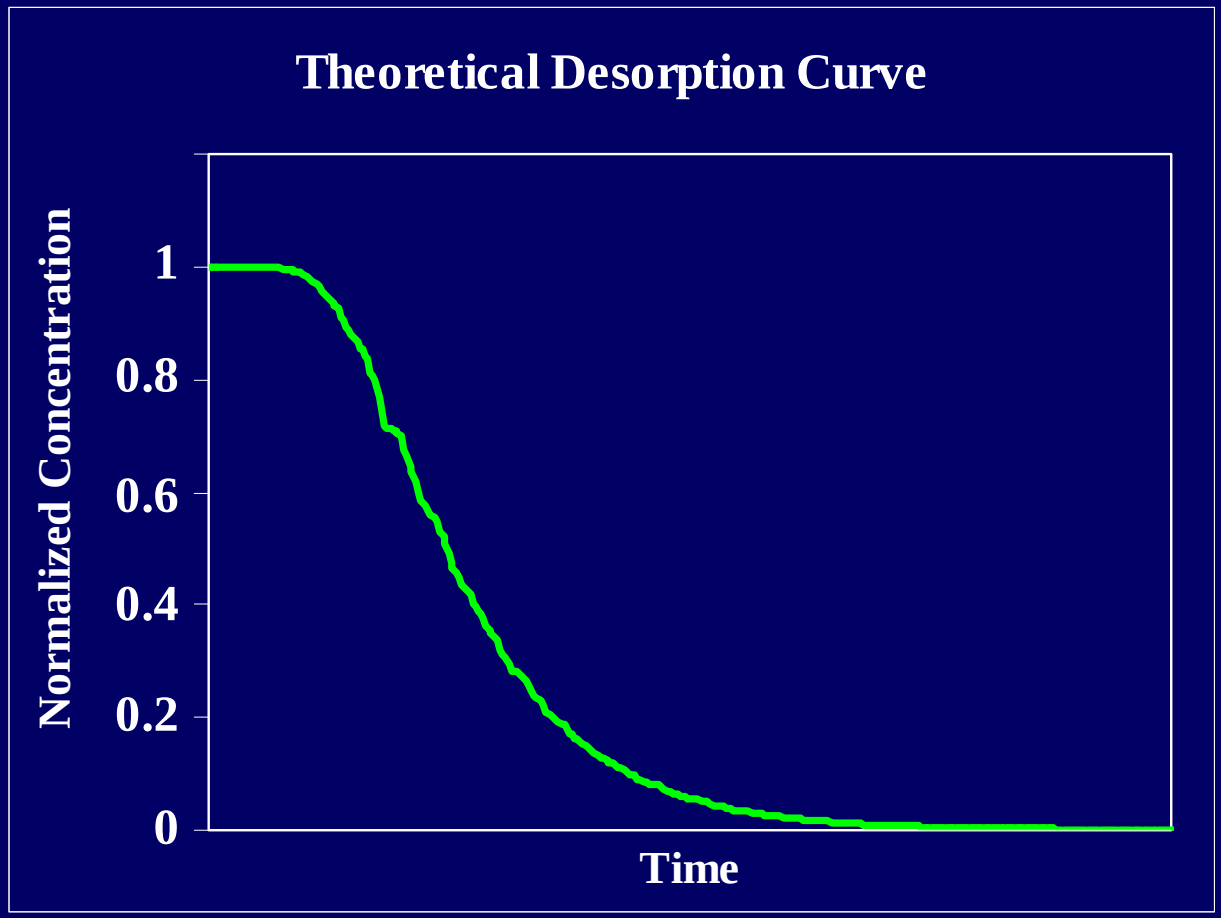
- Desorption of contaminants from downgradient aquifer solids
- Reverse diffusion of contaminants from stagnant/low-permeability zones
- Other processes

Langmuir Sorption Model

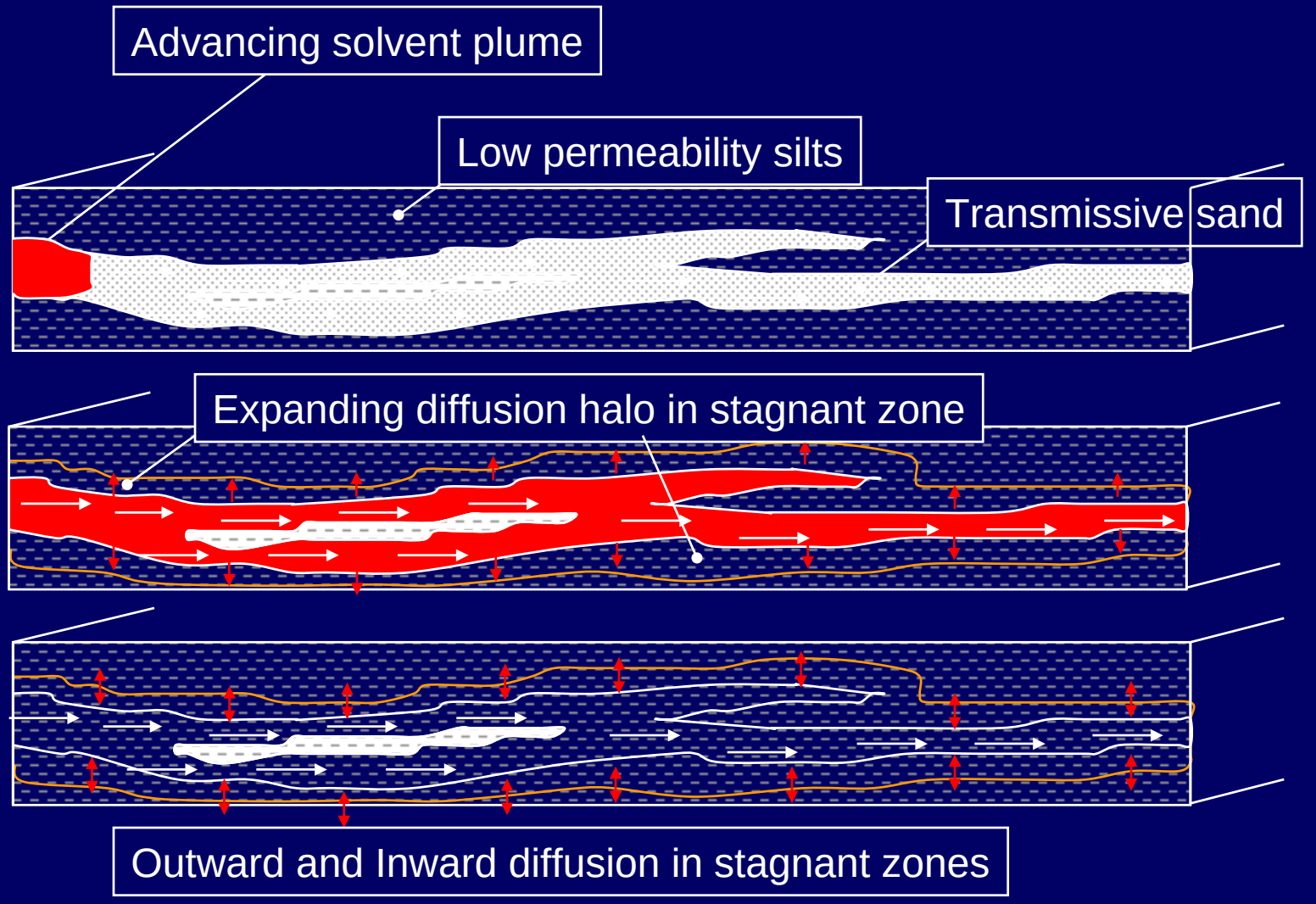
First Order Model:
$v = K_d c_d$
with $K_d = f_{oc} K_{oc}$

$$c_p = mv$$
$$= mK_d c_d$$

$$c_T = c_d + c_p$$
$$= c_d + mK_d c_d$$



Plume Attenuation/ Plume Replenishment by Matrix Diffusion - (after Parker et al.,1994 and 1997)



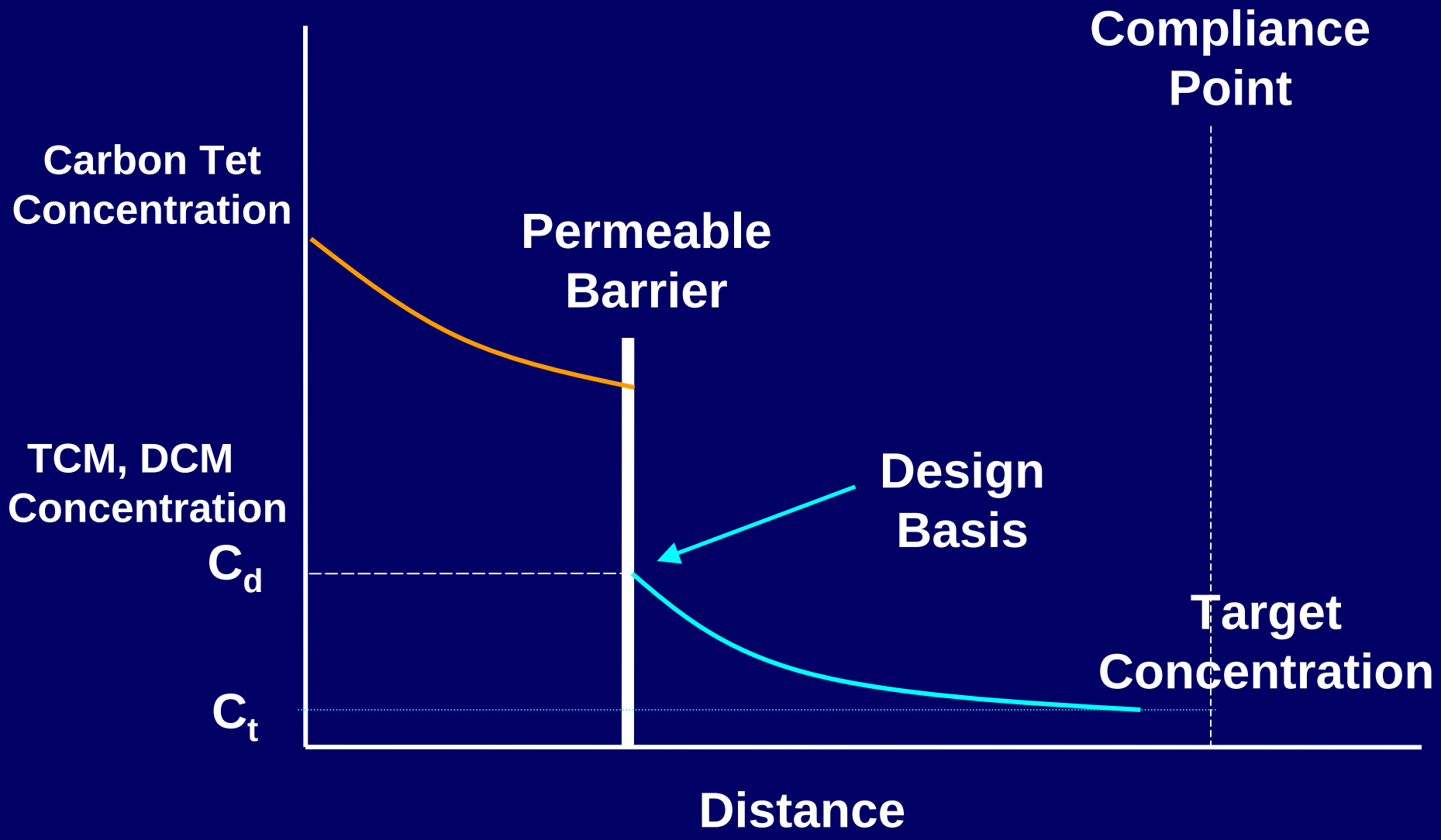
Steady State Processes Contributing Contaminants

- Pass-through of certain chlorinated compounds that are not effectively treated by ZVI such as 1,2 dichloroethane
- Production of stable chlorinated daughter products such as dichloromethane from ZVI treatment of carbon tetrachloride
- Presence of chlorinated contaminants in the PRB effluent
  - **Parent compounds (TCE, PCE, etc.)**
  - **Daughter products (cis 1,2 DCE, VC, TCM, etc.)**

Bottom Line

- There will be downgradient contaminant contribution from the aquifer itself for a significant time (desorption, diffusion, etc.)
- There may be chlorinated contaminants in the treated PRB effluent
- Biodegradation can be a powerful tool for dealing with this “residual” contamination
  - **Natural biological processes**
  - **Engineered / enhanced bioremediation**

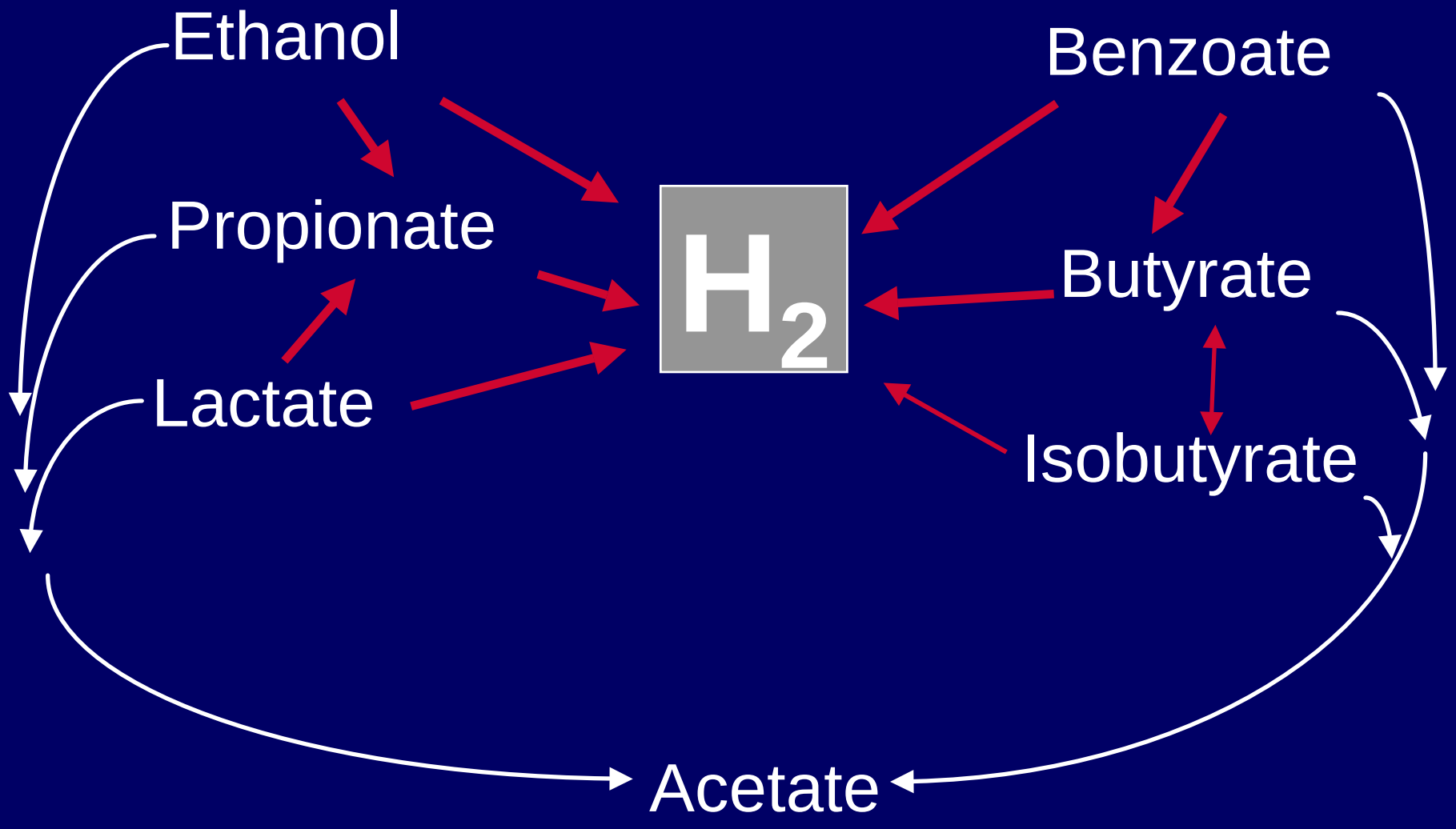
Conceptual Model - PRB with Natural Biodegradation (Steady State)



Overview of Biological Reductive Dechlorination

- Chlorinated solvents used as electron acceptor in bacterial metabolism
- The most important electron donors are **hydrogen** and reduced organic acids
  - **acetate (CH3COOH)**
  - **formate (HCOOH)**
  - **pyruvate**
- More complex organic substrates undergo fermentation to generate electron donors
  - **Lactate, benzoate, etc.**

Donor Fermentation Pathways



Dr Jim Gossett, Cornell University

Fermentation

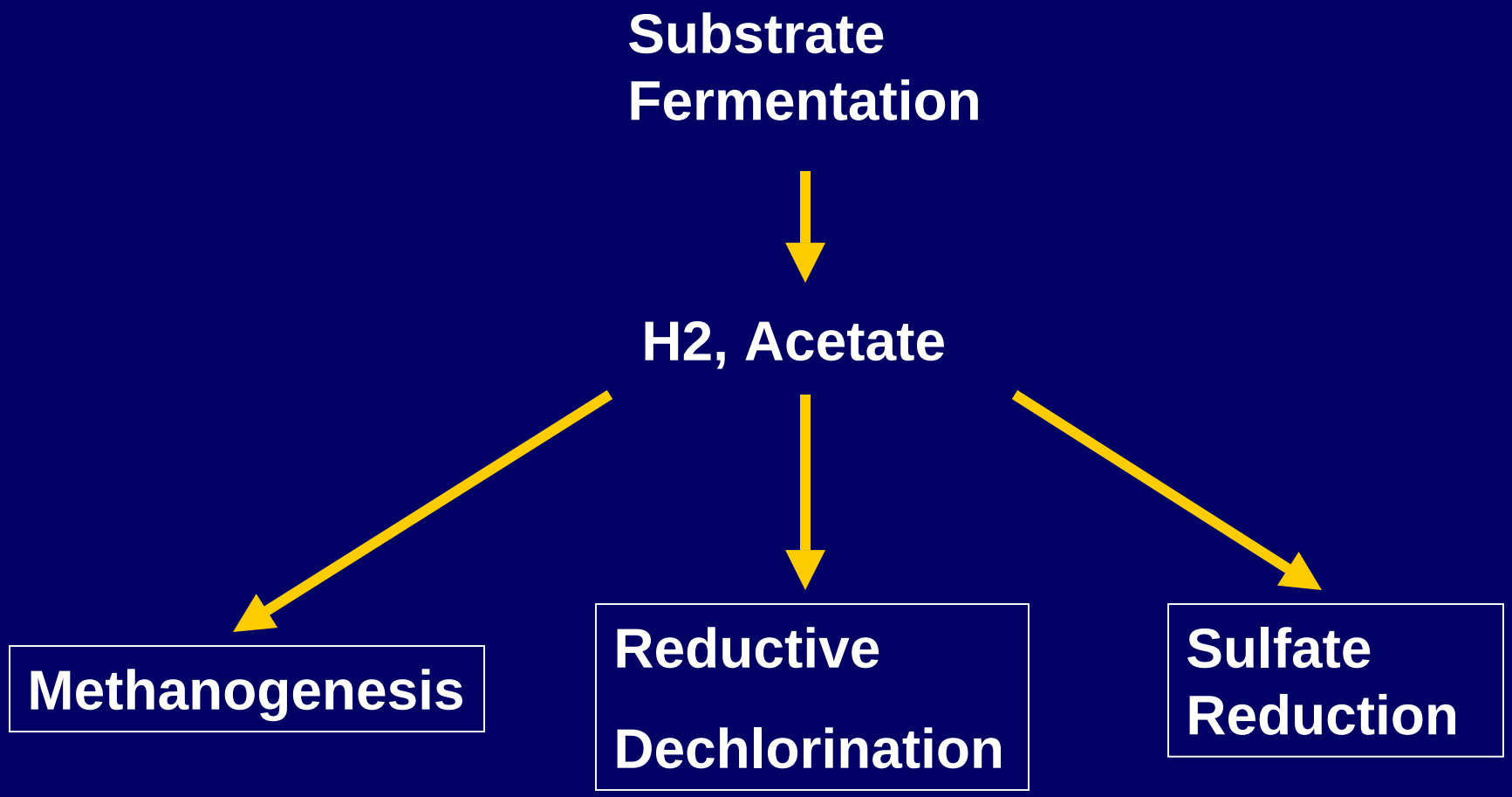
Oxidation of an electron donor in the absence of a separate electron acceptor:

Glucose ($C_6H_{12}O_6$) → 2 Ethanol (C_2H_6O) + 2HCO_3^- + 2H^+

Glucose ($C_6H_{12}O_6$) + 4H_2O → 2 Acetate (CH_3COOH) +2HCO^-_3 + 4H^+ + 4H_2

Methylene Chloride also undergoes fermentation producing acetate and hydrogen!

Bacterial Competition for Hydrogen



Contaminant Biodegradation

- Biodegradation is a function of microbial populations and community structure
- Community structure is dependant on environmental conditions, which give some bacteria a competitive advantage over others:
  - Available electron acceptors
  - Available electron donors
  - Mix of contaminants

Impacts of ZVI on Biodegradation of Chlorinated Compounds

- Creation of geochemical conditions conducive to anaerobic biodegradation
  - Elimination of competing electron acceptors (O2, NO3)
- Production of hydrogen and other electron donors
- Reduction in overall contaminant loading
- Removal of “inhibitory” compounds
- Changing the mixture of contaminants
- Conversion of parent contaminants to more biodegradable daughter compounds

Geochemistry and Electron Acceptors

- Available electron acceptors are used sequentially in the order of energy yield

High energy yield (First used) → **Low energy yield (Last used)**

Oxygen > Nitrate > Fe^{3+} > Sulfate > Methanogenesis

↑

Chlorinated Ethenes

Production of Hydrogen Iron Corrosion Reaction

$$Fe^{0} \longrightarrow Fe^{+2} + 2e^{-}$$

$$2H_2O \longrightarrow 2H^{+} + 2OH^{-}$$

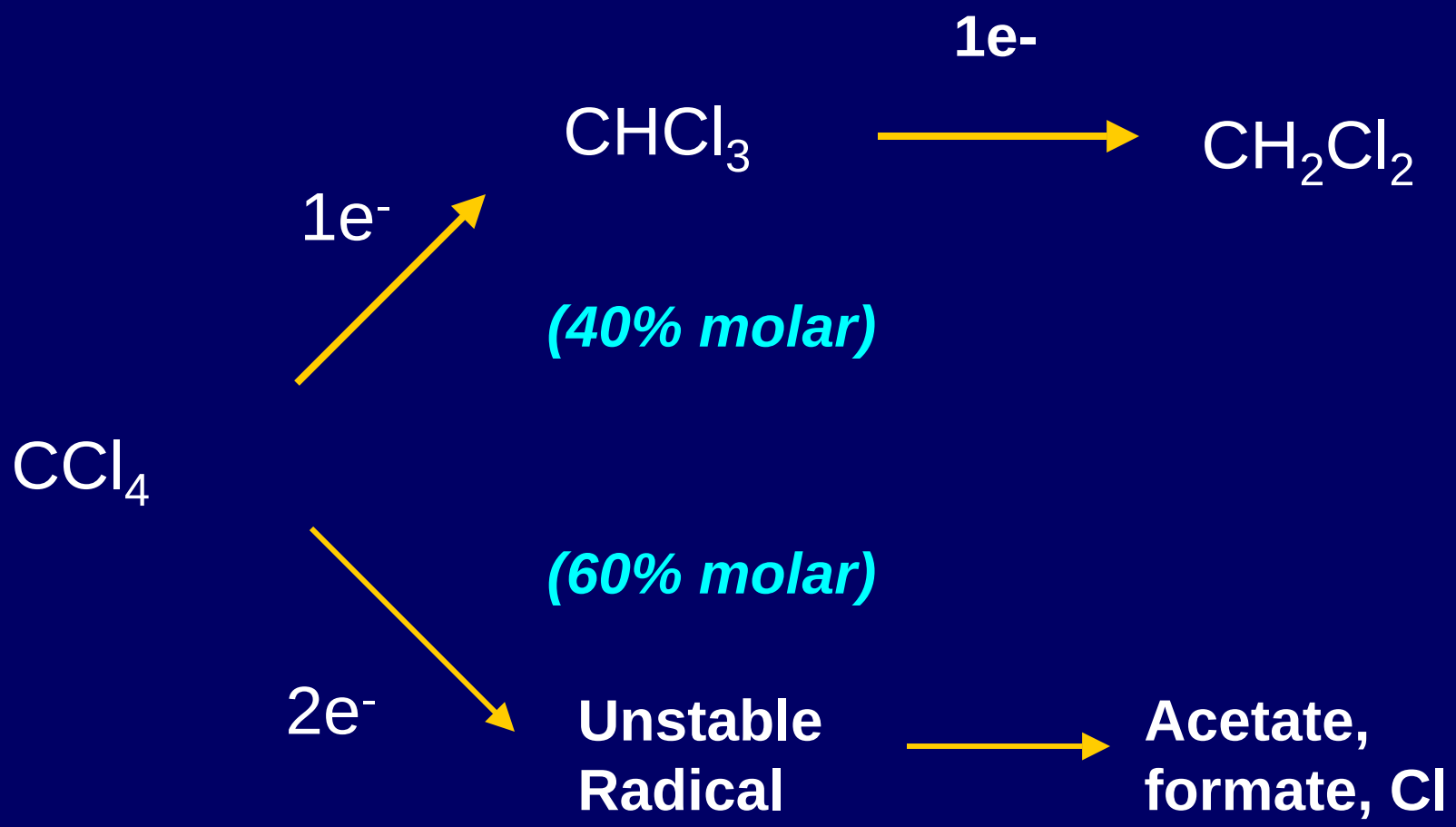
$$2H^{+} + 2e^{-} \longrightarrow H_{2(g)}$$

$$R\text{-}Cl + H^{+} + 2e^{-} \longrightarrow R\text{-}H + Cl^{-}$$

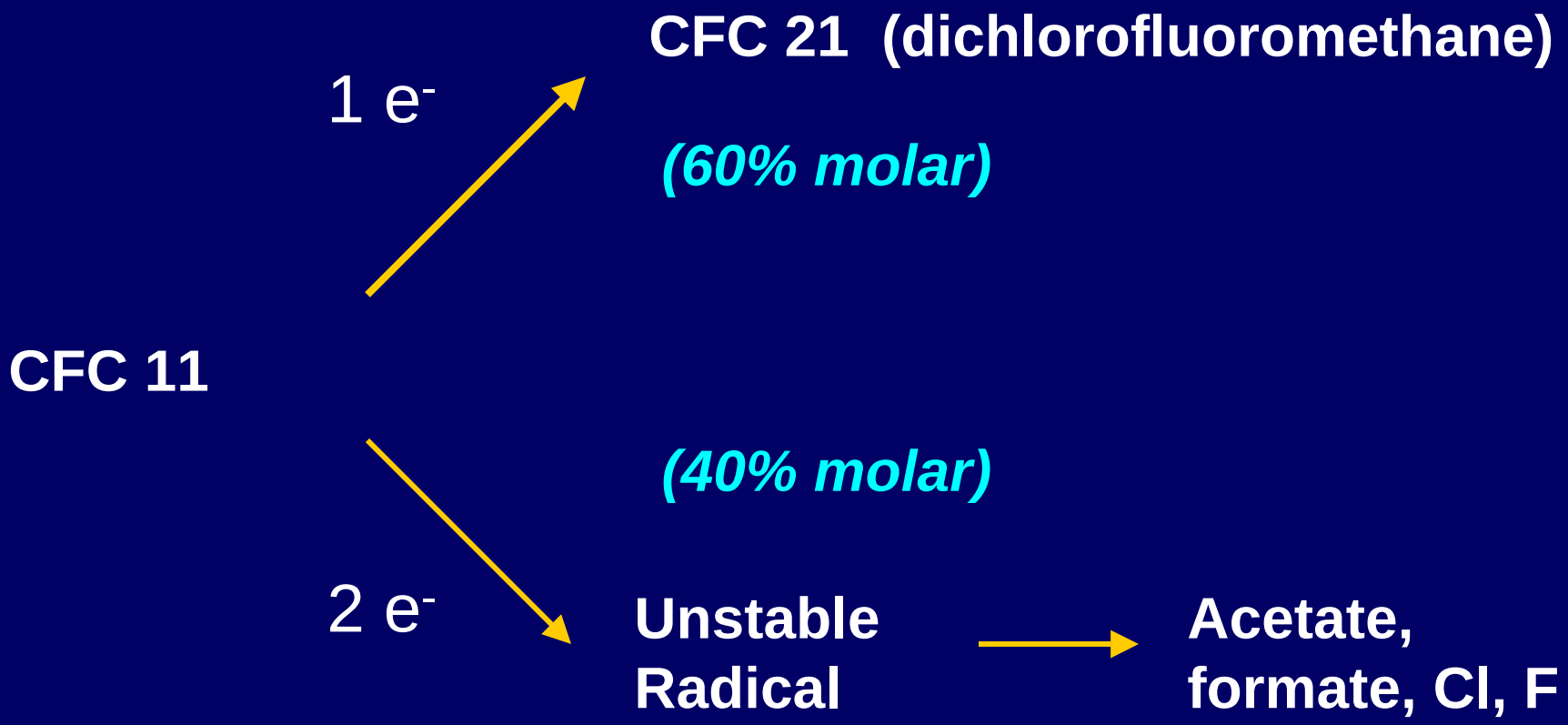
Production of Fully Dehalogenated Daughter Products / Electron Donors

- CT conversion to acetate, formate
  - **Used directly by dehalogenators**
- PCE, TCE conversion to ethene, acetylene
  - **ethene used in cometabolic processes that can result in dechlorination**
- *Direct addition of organic carbon from construction can "jump start" downgradient biodegradation*
  - ***Biodegradable Slurry Trenching***
  - ***Hydraulic Fracturing (guar)***

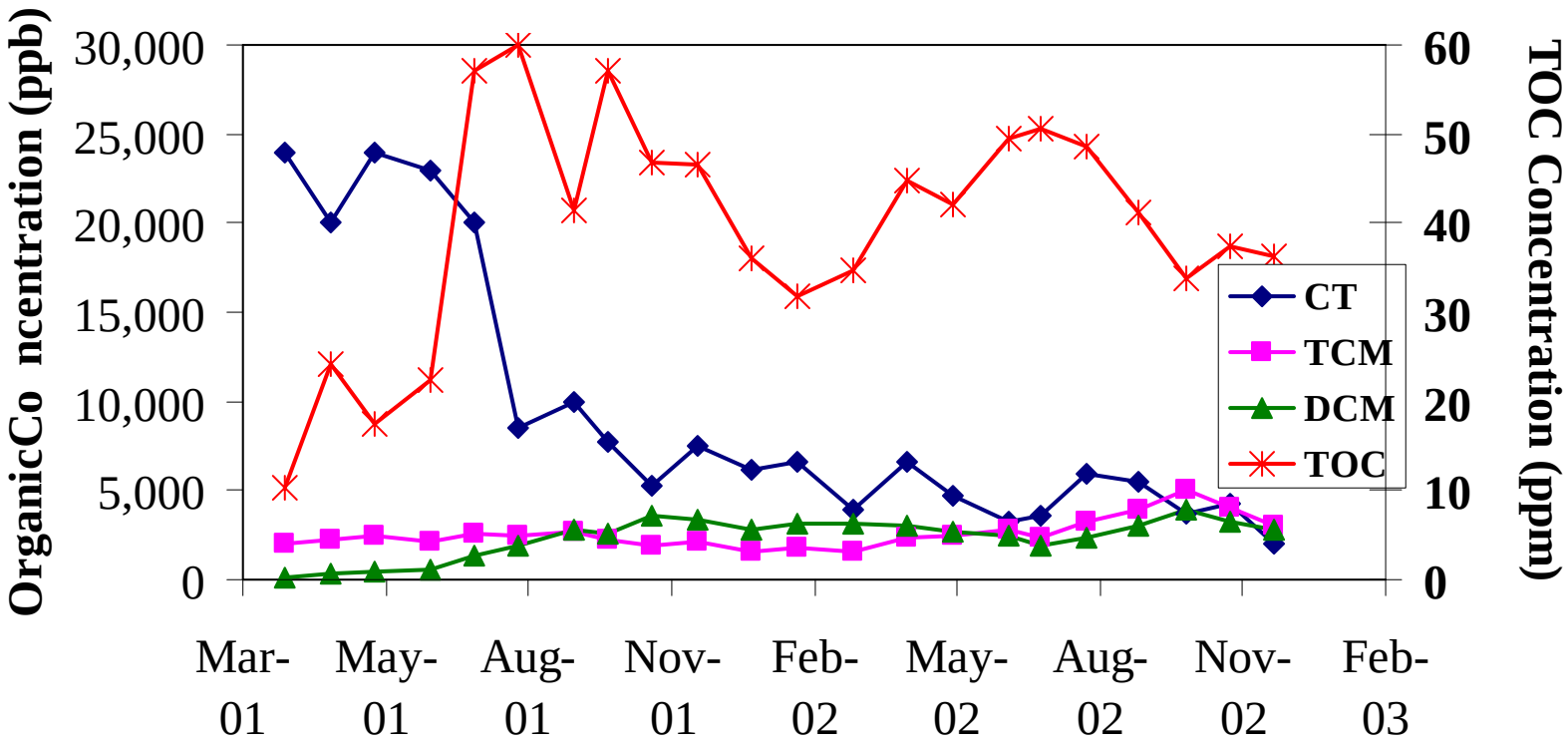
Carbon Tetrachloride Reactions with ZVI

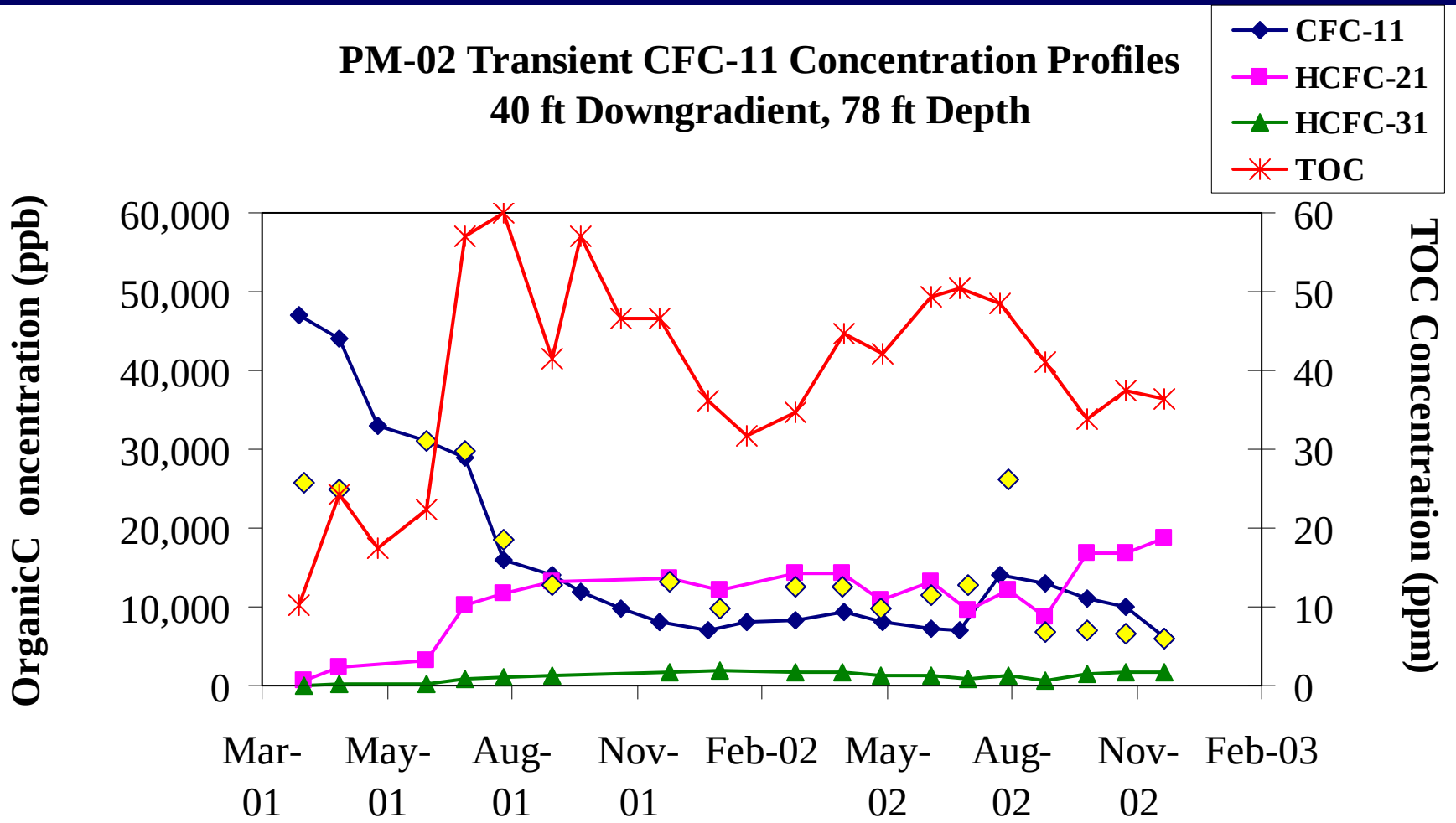


CFC 11 Reactions with ZVI (Trichlorofluoromethane)



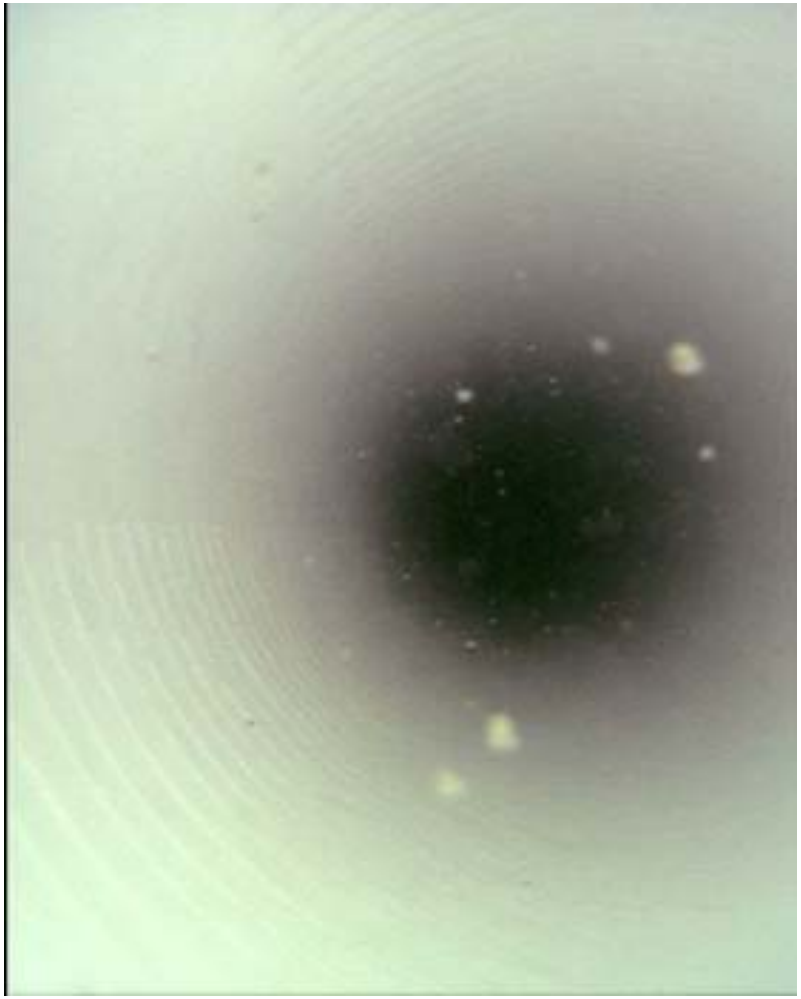
PM-02 Transient Carbon Tetrachloride Concentration Profiles
(40 ft Downgradient, 78 ft Depth)



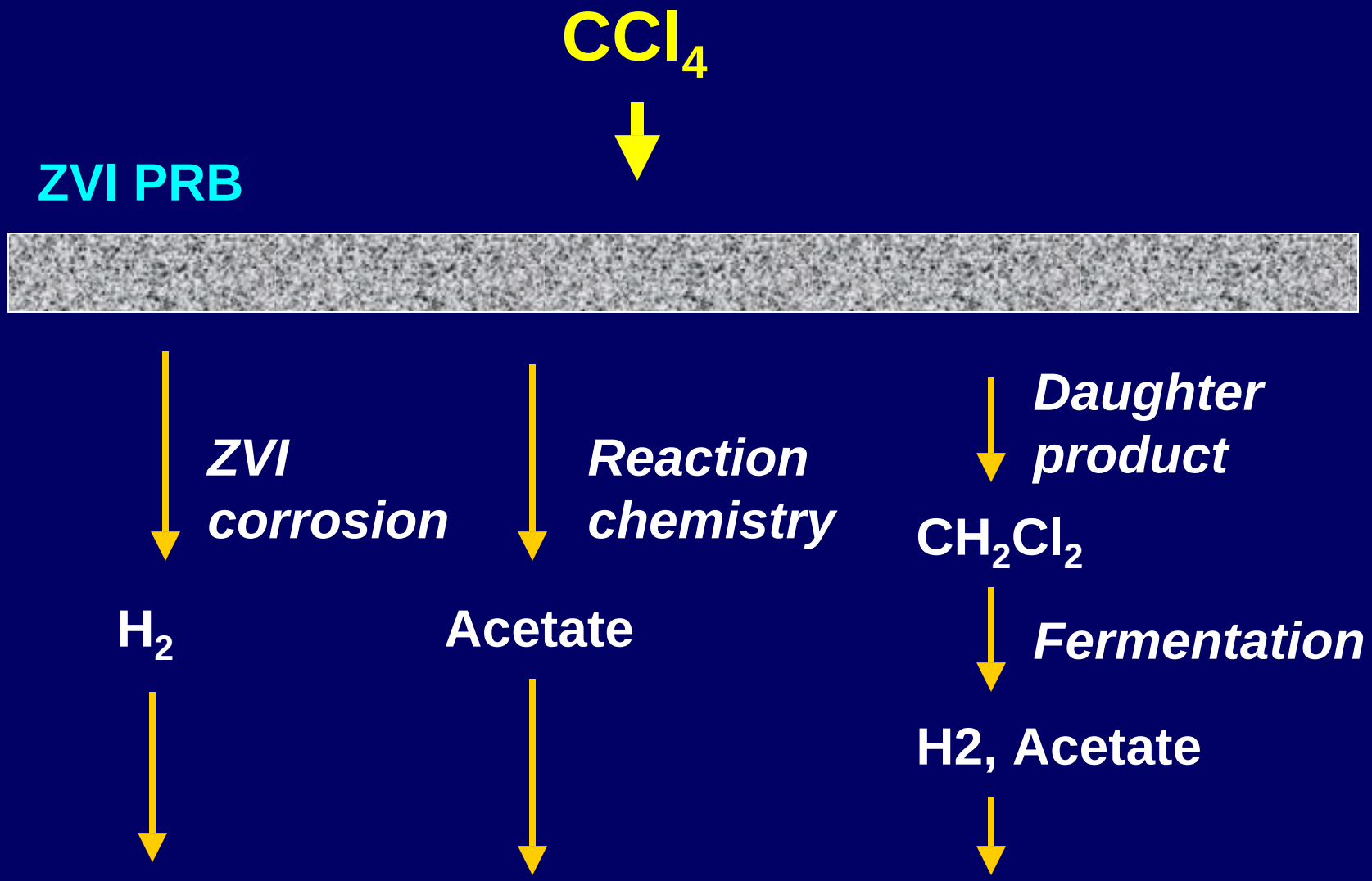

PM-02 Transient CFC-11 Concentration Profiles
40 ft Downgradient, 78 ft Depth
CFC-11
HCFC-21
HCFC-31
TOC
OrganicC oncentration (ppb)
TOC Concentration (ppm)
60,000
50,000
40,000
30,000
20,000
10,000
0
60
50
40
30
20
10
0
Mar-01
May-01
Aug-01
Nov-01
Feb-02
May-02
Aug-02
Nov-02
Feb-03

Sulfate Reduction Induced Downgradient of PRB

Upgradient



Downgradient


CCl_4
ZVI PRB
ZVI corrosion
Reaction chemistry
Daughter product
CH_2Cl_2
H_2
Acetate
Fermentation
H2, Acetate
Reductive Dechlorination, SO4 Reduction, Methanogenesis

Reduction in Overall Contaminant Loading by PRB

- Reduce total contaminant flux to a point where it can be handled by the attenuation capacity of the aquifer
  - **Available electron donor supply**
- Removal of “inhibitory” compounds
  - **TCM known to inhibit reductive dechlorination of chlorinated ethenes**
  - **1,1,1 TCA and CT also thought to inhibit (*may actually be competition*)**

Changing the Contaminant Mix

- As with inorganic electronic acceptors, dechlorinating bacteria will preferentially use RCl electron acceptors in order of available energy
- More accurately, bacteria that utilize the higher energy electron acceptors will out-compete those that use lower energy electron acceptors in a given mix (competition for H_2)
- The microbial population will shift in response to a change in the mix of electron acceptors

Gibbs Free Energy for Common Dechlorination Reactions

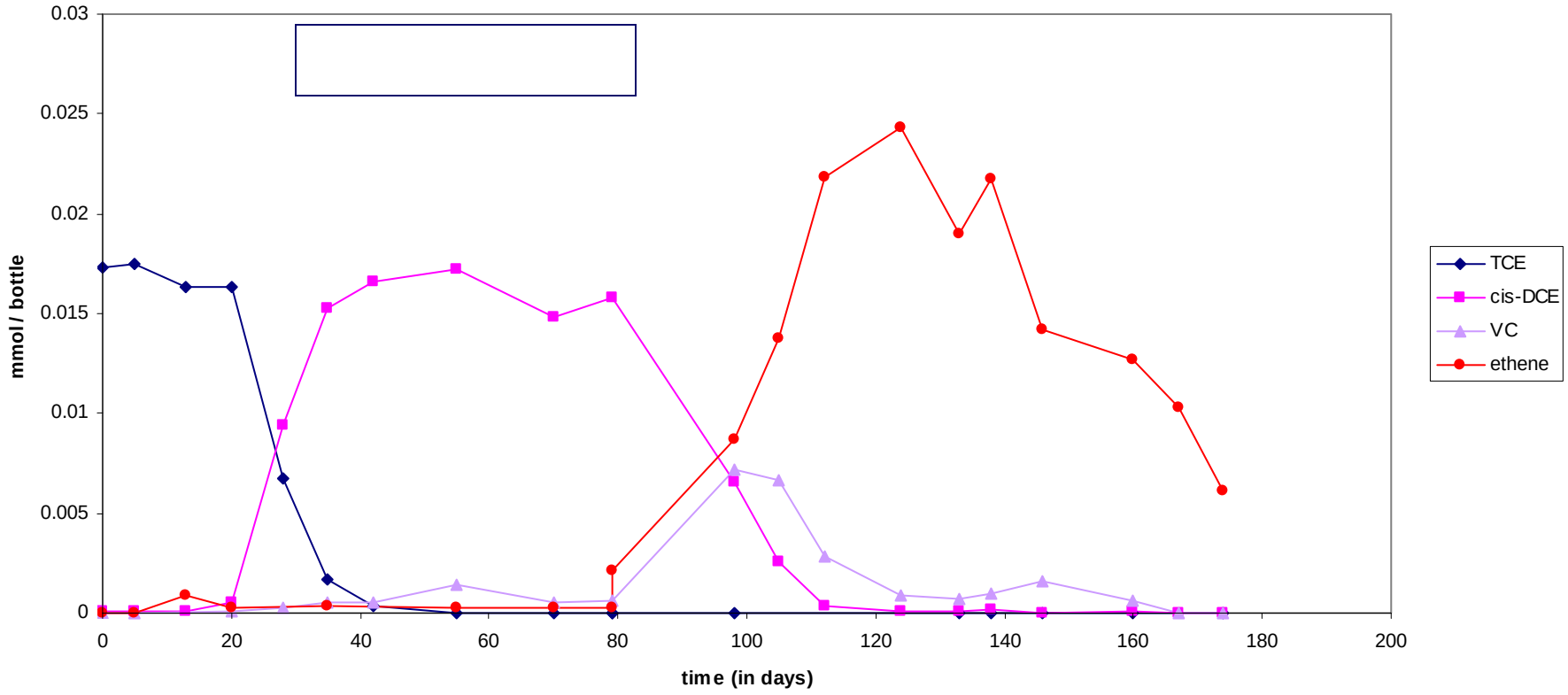
Dechlorination Reaction	Gibbs Free Energy (kilojoules / mole)
PCE => TCE	55.3
TCE => cis-1,2 DCE	53.0
cis 1,2 DCE => VC	38.3
VC => ethene	43.4
CT => TCM	65.0
TCM => DCM	54.0
1,1,1 TCA => 1,1 DCA	54.1
1,1 DCA => CA	44.5

TCE Plume

- TCE → cis 1,2 DCE (*53 kJ/mole*)
- cis 1,2 DCE → VC (*38 kJ/mole*)
- VC → Ethene (*43 kJ/mole*)

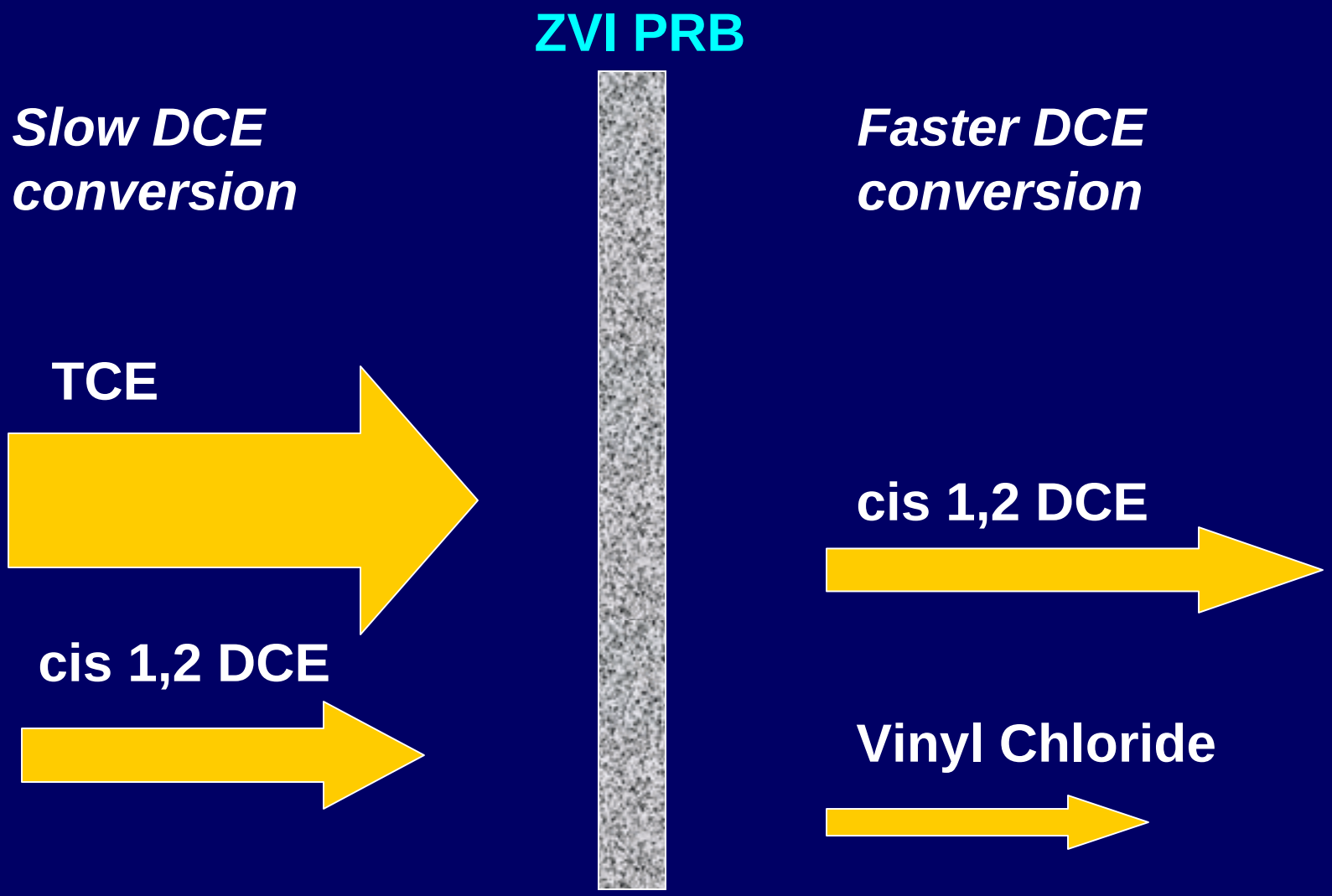
Conversion of cis 1,2 DCE to VC will likely not proceed until all of the TCE is converted

Caldwell Trucking
10 ppm TCE Microcosm



- Half Lives: TCE 2.5 days; cis-DCE 10.4 days; VC 10.7 days

Impact of PRB on Contaminant Mix and Microbial Community Structure

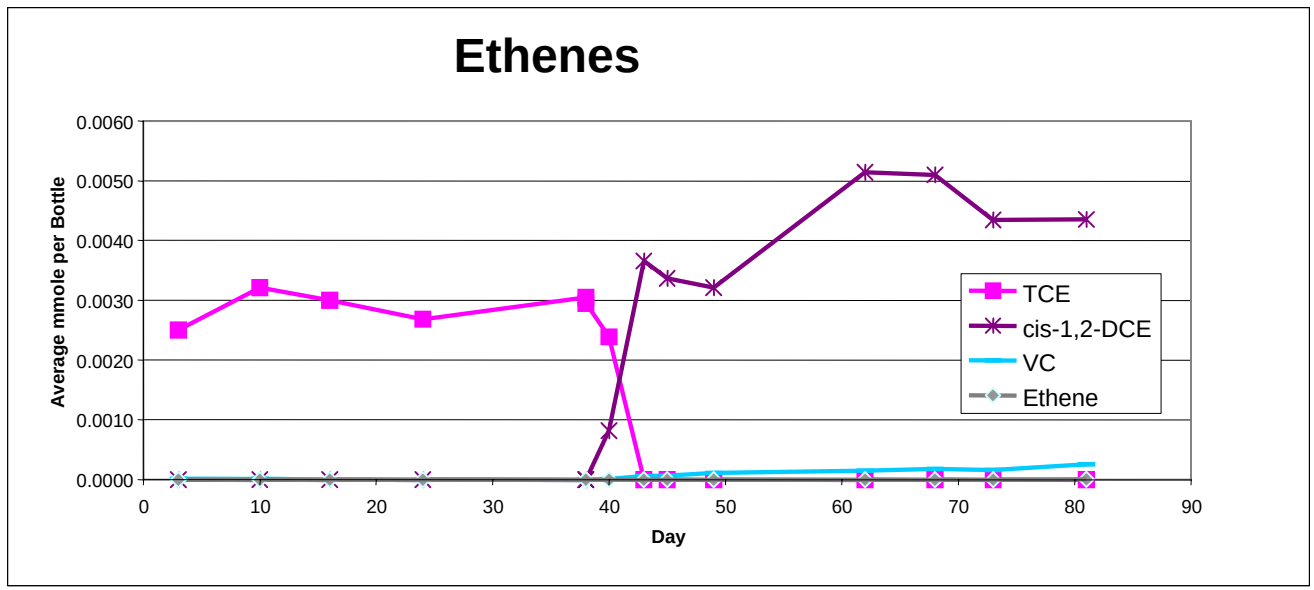


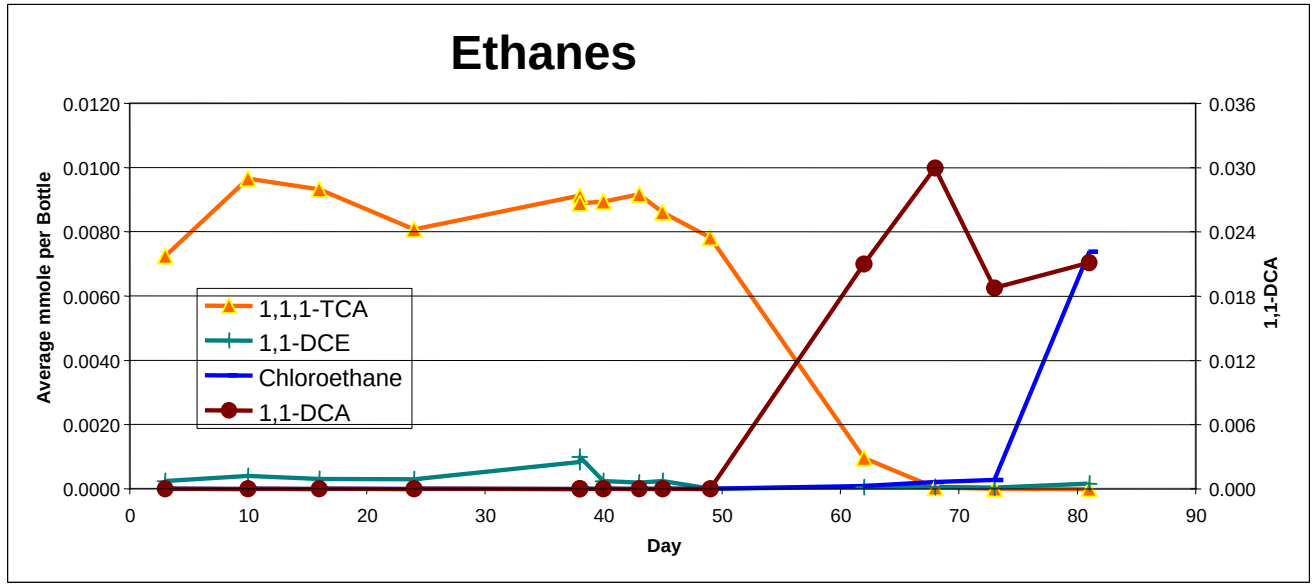
Mixture of TCE, TCA

- TCE → cis 1,2 DCE (*53 kJ/mole*)
- cis 1,2 DCE → VC (*38 kJ/mole*)
- 1,1,1 TCA → 1,1 DCA (*54 kJ/mole*)

Conversion of cis 1,2 DCE to VC will likely not proceed until all of the TCE and TCA is converted

Mixed Chloroethene / ethane Site





Conversion of Contaminants to More Biodegradable Compounds

- Some fully halogenated compounds only biodegrade via reductive dechlorination (PCE, CT)
- Partially dechlorinated daughter compounds may degrade via a variety of pathways
  - **Reductive dechlorination (cis 1,2 DCE, VC)**
  - **Anaerobic oxidation (cis 1,2 DCE, VC)**
  - **Cometabolic (TCE, cis 1,2 DCE, TCM, DCM)**
  - **Aerobic oxidation (cis 1,2 DCE, VC, DCM)**
  - **Fermentation (DCM, VC)**

Closing Thoughts

- A PRB alters environmental conditions in the aquifer, resulting in shifts in microbial community structure and resultant contaminant biodegradation
- PRB and biodegradation can / should be considered as parts of an integrated remediation system design
- Biostimulation and bioaugmentation can be done downgradient of a PRB to enhance contaminant biodegradation if baseline attenuation capacity is not sufficient

Conceptual Model
PRB with Enhanced Biodegradation