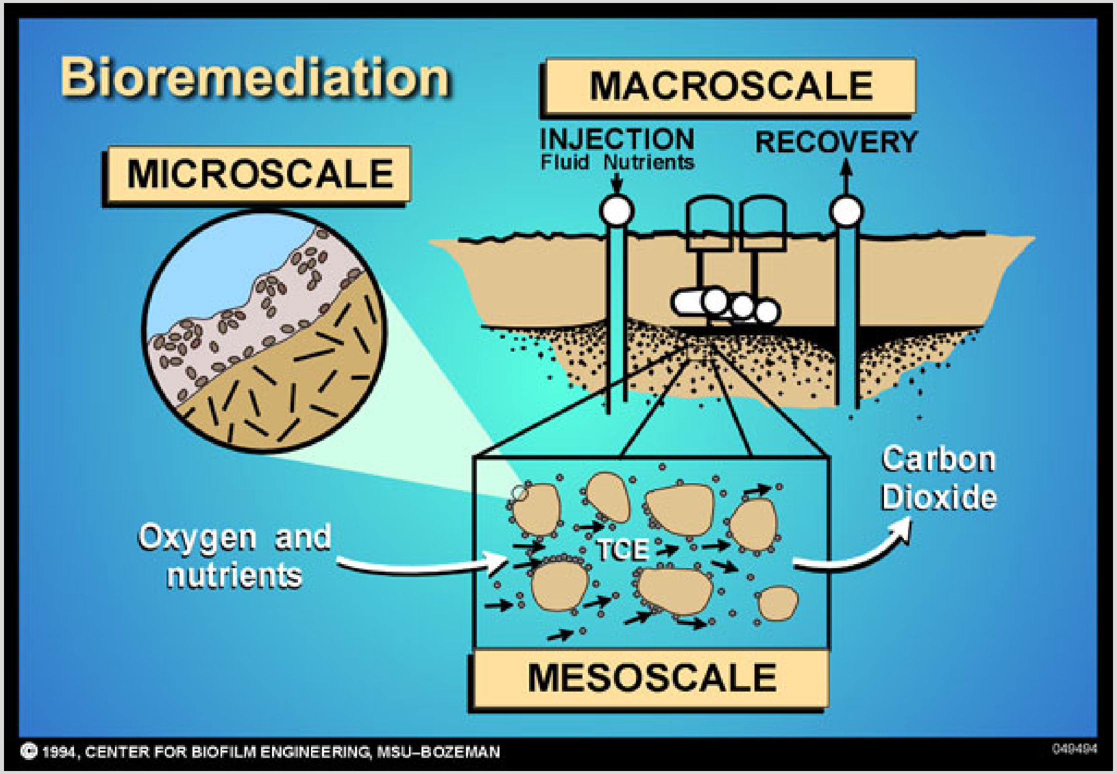


In Situ Biodegradation/Natural Attenuation in Soil and Ground Water

Paul Sturman, PhD, PE

In Situ Biodegradation & Natural Attenuation of Organic Contaminants in Groundwater

- Reduction in contaminant mass as a result of the activity of microorganisms
- Occurs in virtually all soil/groundwater systems (extent and rate may vary considerably).
- Natural Attenuation includes both biotic and abiotic processes

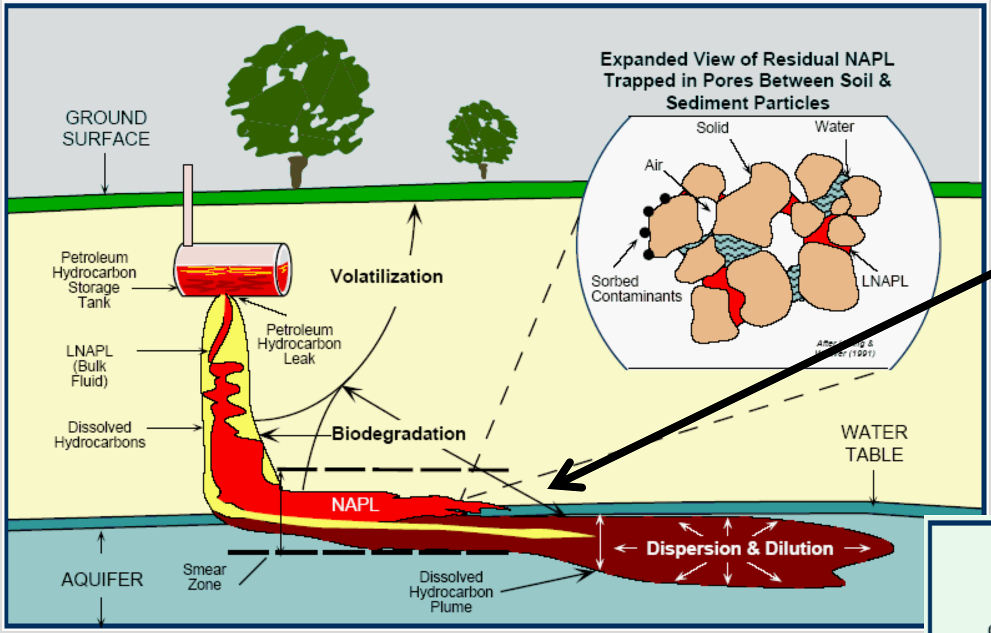
Lines of Evidence to show Natural Attenuation/ Biodegradation is occurring:

- Natural Attenuation - Historical groundwater contaminant level data that demonstrates a clear trend of decreasing contaminant mass
- Biodegradation - Hydrogeologic and geochemical data that demonstrates (indirectly) the types of bacterial processes active at the site;

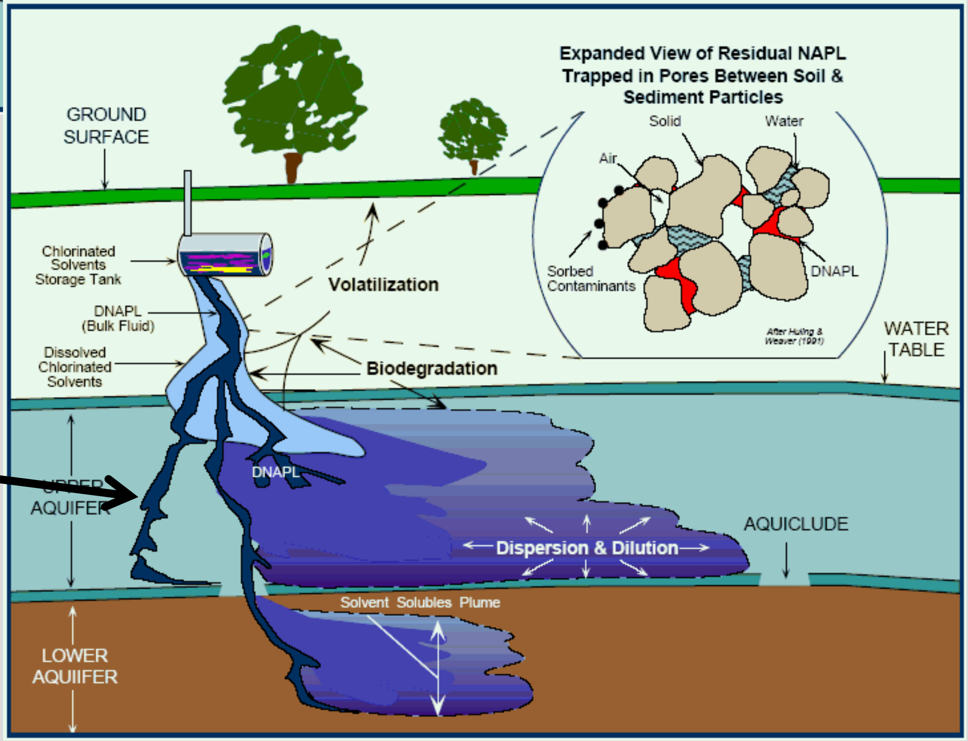
Organic Contaminant Classes

	Examples	Properties
Petroleum Hydrocarbons	BTEX, MTBE, Alkanes, PAHs	Highly soluble to insoluble, typically biodegradable (except MTBE), form floating NAPL
Chlorinated Solvents	PCE, TCE, DCE TCA, DCA	Highly soluble, biodegradable under narrow range of conditions form DNAPL
Wood treatment wastes & other organic compounds	Pentachlorophenol PCBs, dioxin	Insoluble, typically recalcitrant

Types of Plumes

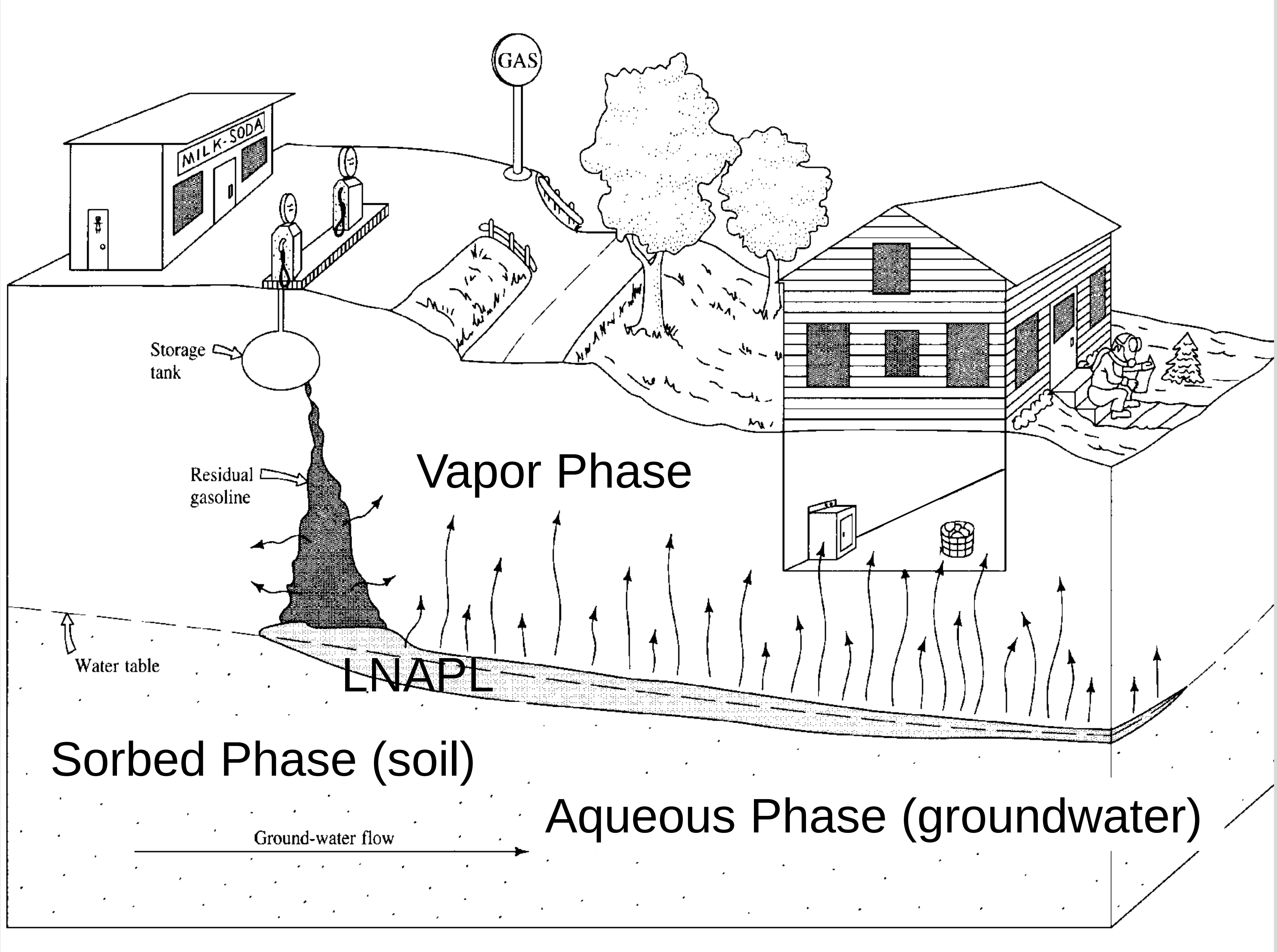


LNAPL – light non-aqueous phase liquid



DNAPL – dense non-aqueous phase liquid

Phase Equilibrium



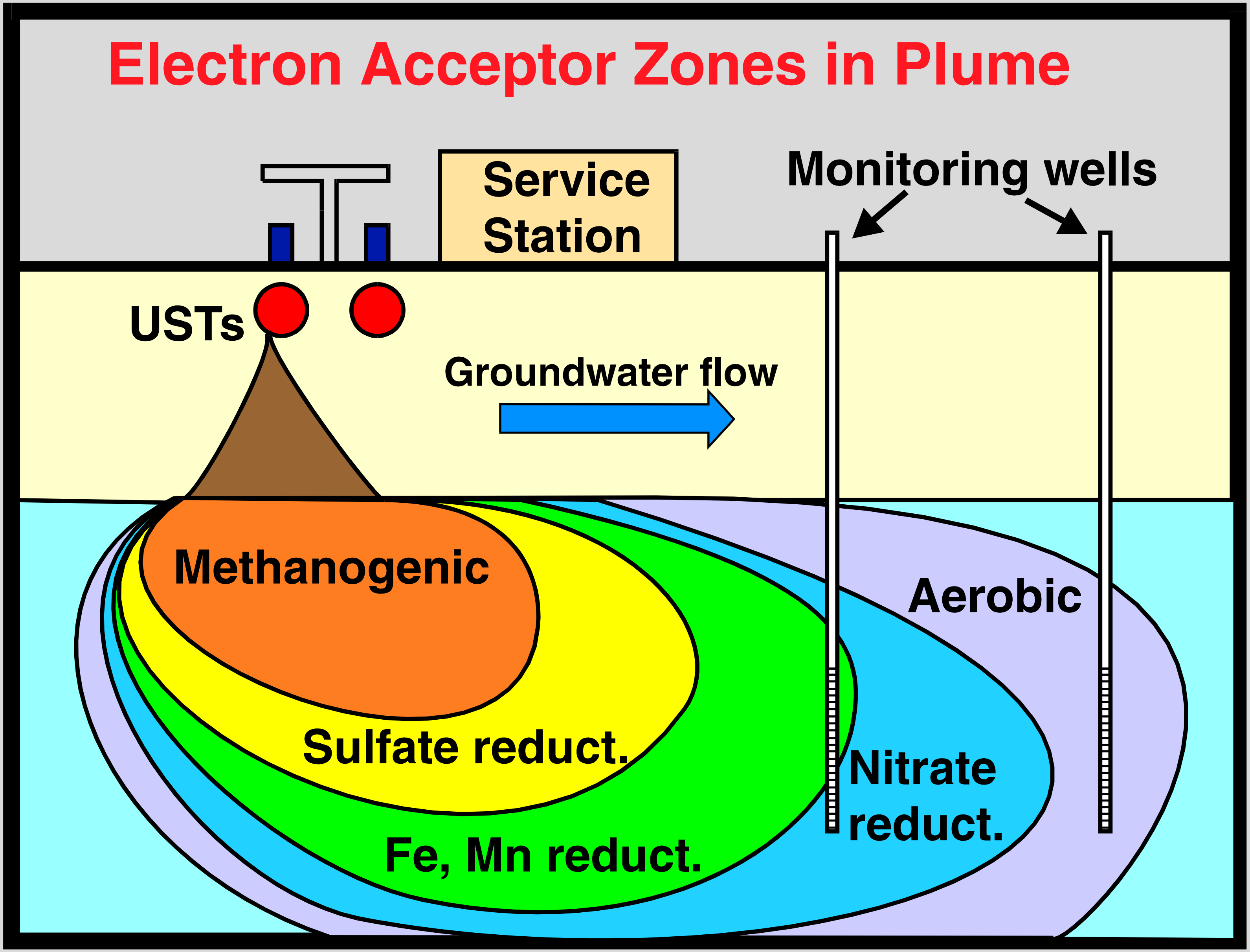
Necessary constituents for biodegradation:

- Bioavailable organic compounds
- Microorganisms capable of degrading target compounds
- Electron acceptors (O_2, NO_3, Fe^{+3}, Mn^{+4}, SO_4, CO_2)
- Necessary nutrients (N, P, K)

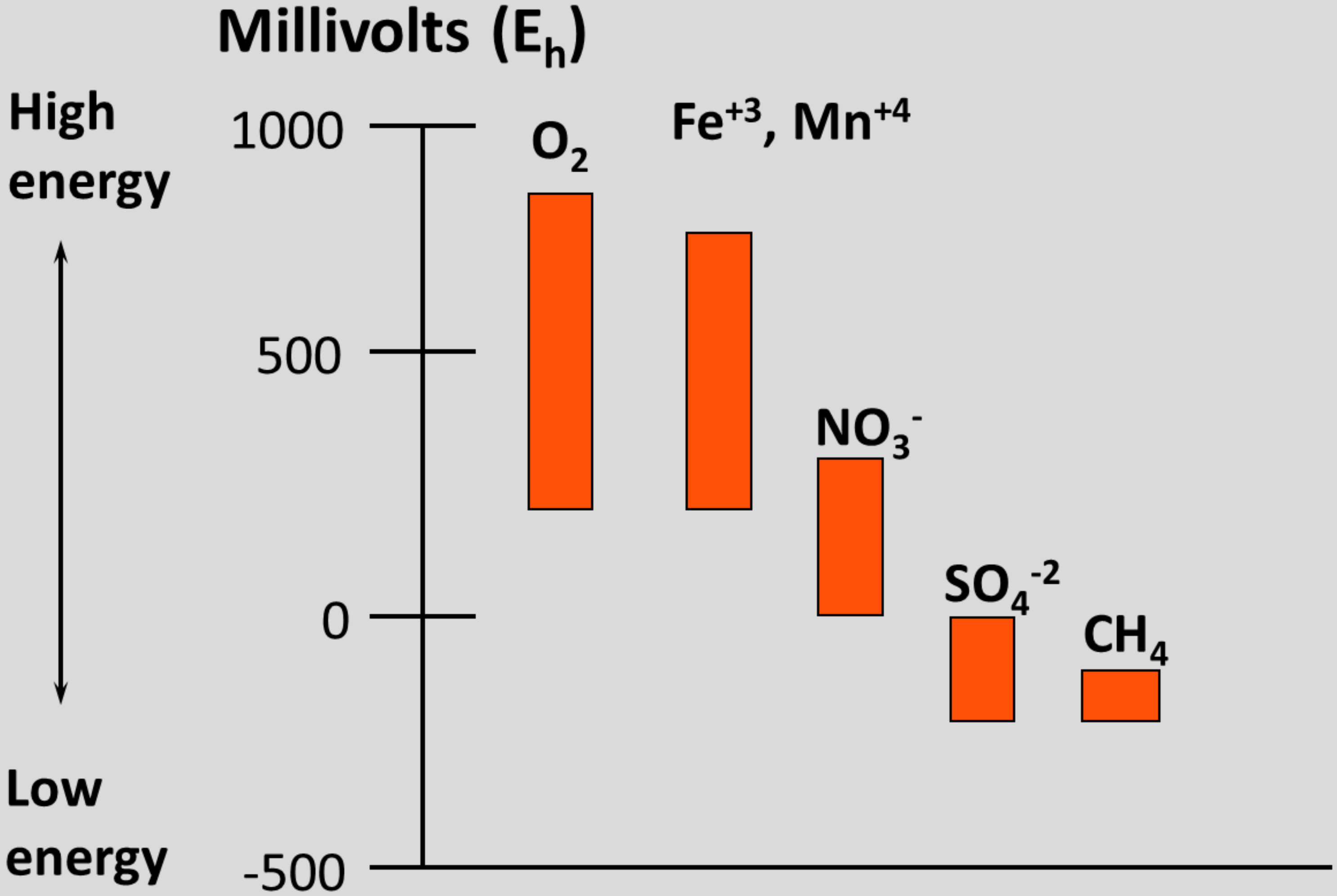
Energy Available from Electron Acceptor Processes

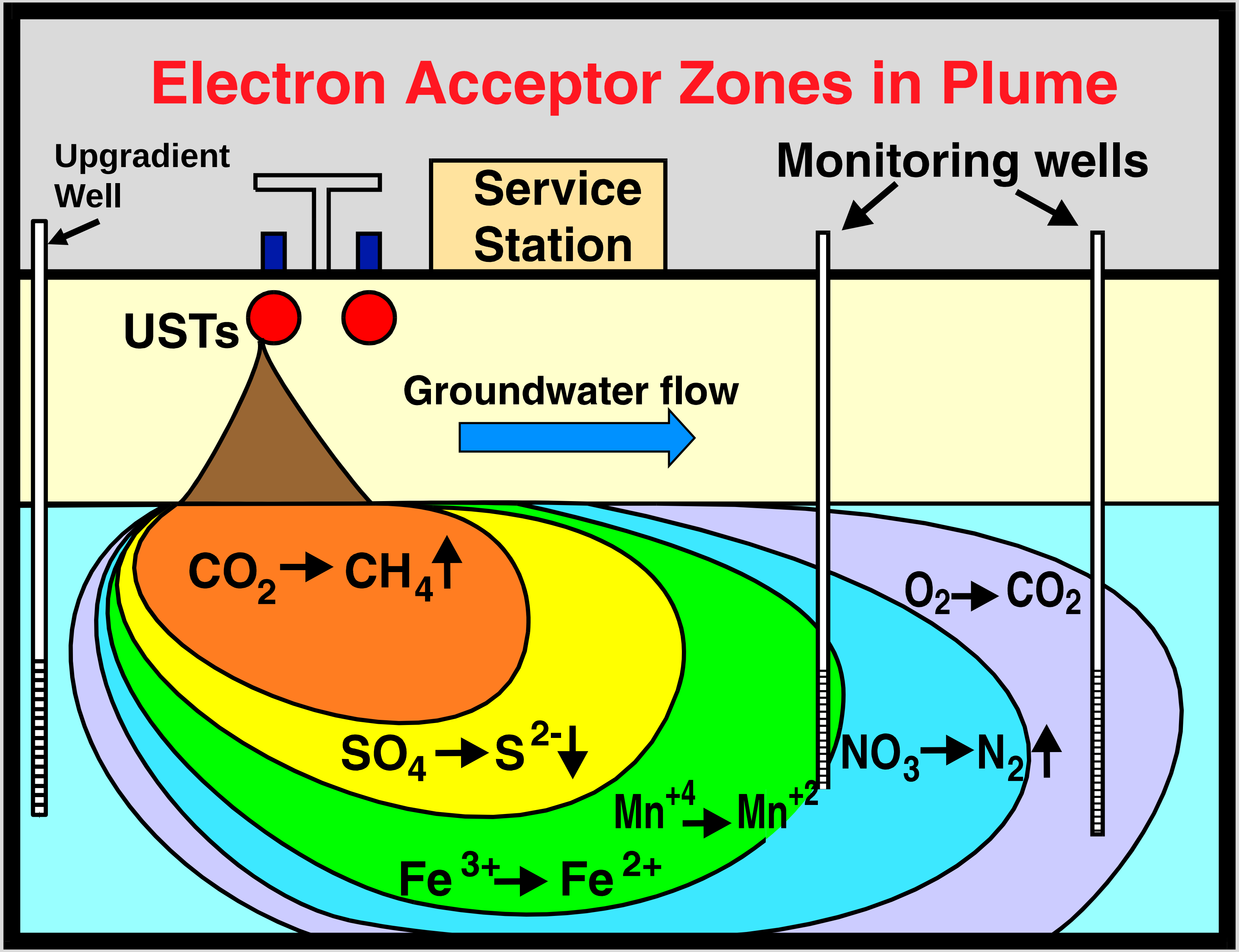
Electron Acceptor	ΔG^o (kJ/mol mineralized) Toluene	Benzene
O_2	-3913	-3566
NO_3^-	-3778	-3245
Fe^{+3}, Mn^{+4}	~ -2175	~ -2343
SO_4^{-2}	-358	-340
CO_2	-37	-136

ΔG^o = Gibbs free energy


Electron Acceptor Zones in Plume
Service Station
Monitoring wells
USTs
Groundwater flow
Methanogenic
Aerobic
Sulfate reduct.
Nitrate reduct.
Fe, Mn reduct.

Redox Potential of Biodegradation Reactions





Electron Acceptor Zones in Plume
Upgradient Well
Service Station
Monitoring wells
USTs
Groundwater flow
$CO_2 \rightarrow CH_4 \uparrow$
$O_2 \rightarrow CO_2$
$SO_4 \rightarrow S^{2-} \downarrow$
$NO_3 \rightarrow N_2 \uparrow$
$Mn^{+4} \rightarrow Mn^{+2}$
$Fe^{3+} \rightarrow Fe^{2+}$

Estimating Biodegradation based on Stoichiometry

Using benzene as the model compound

Aerobic Respiration:

$$C_6H_6 + 7.5\ \underline{\mathbf{O_2}} \longrightarrow 6\ CO_2 + 3\ H_2O$$

red text is measurable constituent

Stoichiometric equations from Borden, et.al., 1995

Estimating Biodegradation based on Stoichiometry

Anaerobic Respiration:

Nitrate reduction

$$C_6H_6 + 6\ \underline{NO_3^-} + 6\ H^+ \longrightarrow 3\ N_2 + 6\ CO_2 + 6\ H_2O$$

Iron Reduction

$$C_6H_6 + 30\ Fe(OH)_3 + 6\ H^+ \longrightarrow 30\ \underline{Fe^{+2}} + 6\ CO_2 + 78\ H_2O$$

red text is measurable constituent

Estimating Biodegradation based on Stoichiometry

Anaerobic Respiration:

Sulfate Reduction

$$C_6H_6 + 3.75\ \underline{SO_4}^{-2} \longrightarrow 3.75\ H_2S + 6\ CO_2 + 3\ H_2O$$

Methanogenesis

$$C_6H_6 + 4.5\ H_2O + x\ CO_2 \longrightarrow 3.75\ \underline{CH_4} + 2.25\ CO_2$$

red text is measurable constituent

Electron Acceptors : Benzene Ratio

Electron Acceptor	Molar Ratio	Mass Ratio	
O_2	7.5	3.1	(mass O_2 utilized) / (mass benzene degraded)
NO^-_3	6	4.8	(mass NO_3 utilized) / (mass benzene degraded)
Fe^{+3}	30	22	(mass Fe^2 produced) / (mass benzene degraded)
SO_4^{-2}	3.75	4.6	(mass SO_4 utilized) / (mass benzene degraded)
CH_4	3.75	0.77	(mass CH_4 produced) / (mass benzene degraded)

Typical Ranges of Electron Acceptors (or products) in Ground Water

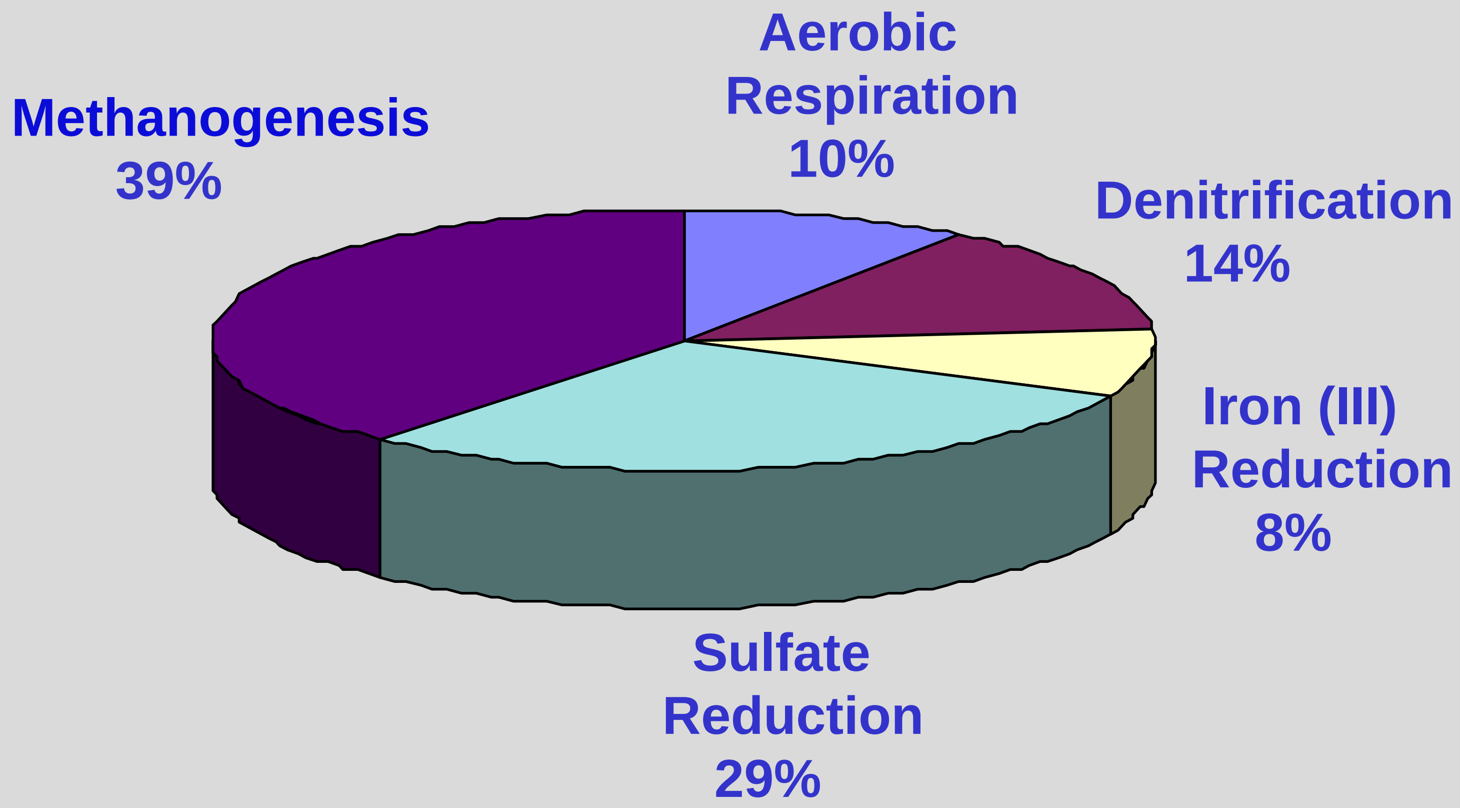
Electron Acceptor	Concentration (mg/l)	
O_2	0-8	
NO_3^-	0-10	
Fe^{+2}	0-50	(reaction product)
SO_4^{-2}	1-150	
CH_4	0-10	(reaction product)

Example Calculation of Assimilative Capacity

Electron Acceptor	Conc. (mg/l)	÷	Mass Ratio	=	Assimilative Capacity (mg/l)
O_2	5		3.1		1.6
NO^-_3	7		4.8		1.5
Fe^{+2}	20		22		0.9
SO_4^{-2}	50		4.6		11.1

Total = 16.5 mg/l

Relative Importance of electron acceptor processes at 25 Air Force Sites



Source: Wiedemeier et al., 1999

Modeling Natural Attenuation

- **Purpose:**
  Use field data to derive observed contaminant removal rate.

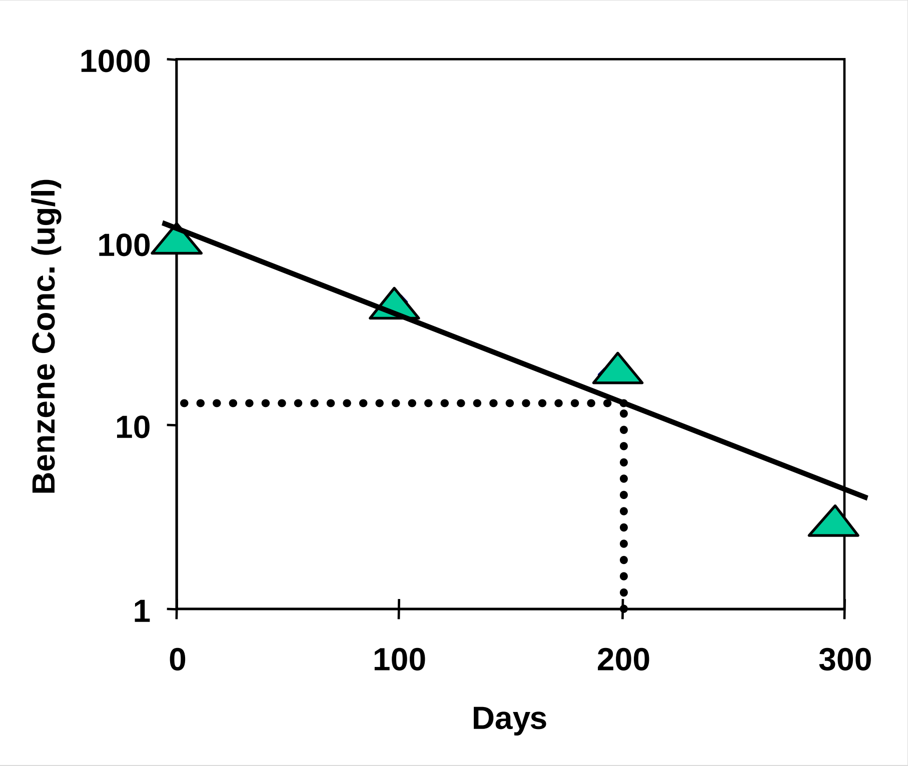
- **Methods:**
  1) Single well concentrations over time.
  2) Multiple well concentrations over distance (same time).
  3) Electron acceptor consumption.

When Each Modeling Method is Useful

- **Single well over time:**
  - Decreasing concentrations over time in one or more wells
  - No free product present in well
- **Multiple well over distance:**
  - Stable plume conditions over time
  - Minimum of 3 monitoring wells along the direction of ground water flow
  - Ground Water velocity can be estimated

Source: Buscheck and Alcantar, 1995

Single Well Over Time



$$C_t = C_0 e^{-[kt]}$$

Y intercept = C_0 (μg/l)
k = 1st order removal rate constant [1/t]

Solve for:

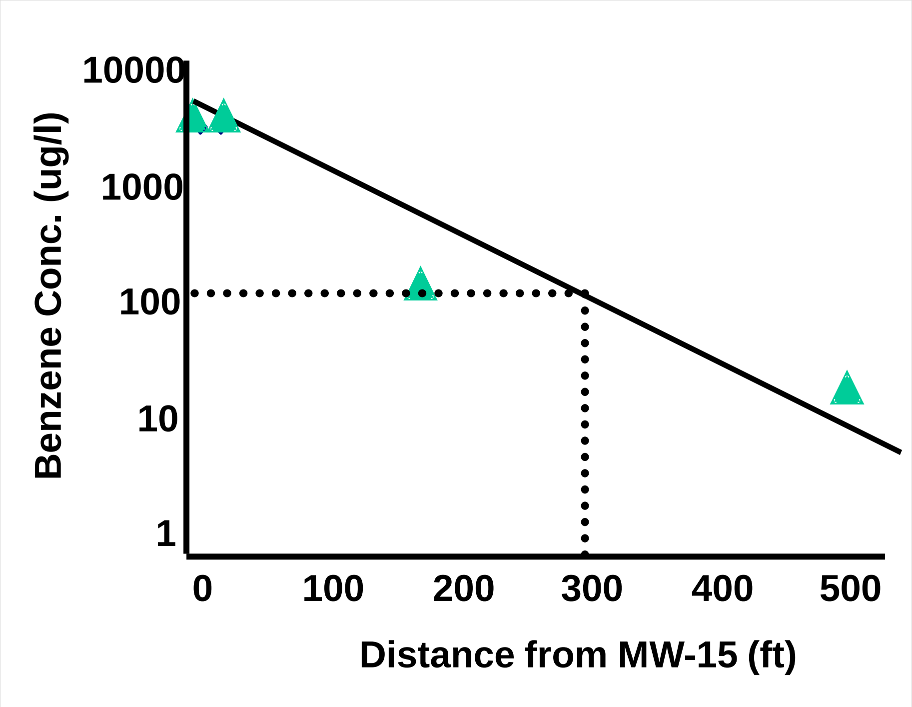
$$k = \frac{\ln(C_0/C_t)}{t}$$

Benzene mass removal rate = $C_t k$ (μg/l/day)

Example: C_0 = 120 μg/l at t = 200 days, C_t = 15 μg/l, then k = 0.010 d^{-1}

Benzene mass removal rate = (15 μg/l)(0.010/day) = 0.15 μg/l/d

Multiple Well Over Distance



$$C_x = C_0 e^{-[kx/v]}$$

x = distance (feet)

v = GW velocity(ft/day)

(seepage velocity)

Y Intercept = C_0 (ug/l)

Solve for:

$$k = v/x\,[\ln(C_0/C_x)]$$

Example: C_o = 5000 μg/l, v = 0.05 ft/day, k = 0.0006/day

at x = 300 ft, C_x = 100 μg/l

Benzene mass removal rate at x=300 ft = (100 μg/l)(0.0006/day)

= 0.06 μg/l/day

Calculation of Hydrocarbon Destruction via Electron Acceptor Consumption

- Estimate groundwater flux through plume area (volume per unit time)
- Establish upgradient and downgradient electron acceptor concentrations (mg/l)
- Determine rate of electron acceptor consumption in plume (mass per unit time)
- Calculate rate of hydrocarbon destruction using stoichiometric equations (mass per unit time)

Stoichiometric Conversion Example: Nitrate Reduction

- $C_6H_6 + 6\ NO_3^- + 6\ H^+ \longrightarrow 3\ N_2 + 6\ CO_2 + 6\ H_2O$
- **Assume 4 mg/l NO_3 observed in aquifer upgradient from plume**
- **Calculate hydrocarbon consumed per unit volume:**

$$(4\ \text{mg/l}\ NO_3\ \text{consumed}) \left(\frac{1\ \text{mg BTEX}}{4.8\ \text{mg}\ NO_3} \right)$$

= **0.83 mg/l BTEX consumed in aquifer**

- **Calculate groundwater flux and total BTEX consumed:**

<u>Assume:</u>

V_{gw} = 0.3 m/day (seepage velocity)

Plume width = 30 m

Plume height = 4 m

Porosity (η) = 0.25

Flux = vwhη = 9 m^3/d = 9x10^3 l/d

BTEX consumed = (9x10^3 l/d) (0.83 mg/l)

= <u>7.5 g BTEX/day</u>

Natural Attenuation of Chlorinated Solvents

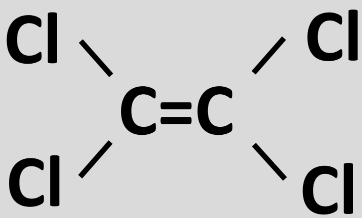
- Not as well accepted as a remedial option
- Different regulatory structure from Petroleum
- Compounds much more recalcitrant than fuel hydrocarbons

but….

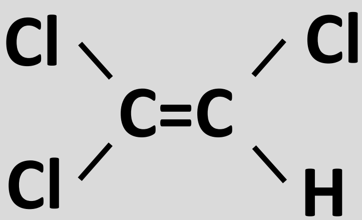
- Natural Attenuation does occur, and recognizing it may assist other remedial efforts

Common Chlorinated Solvents

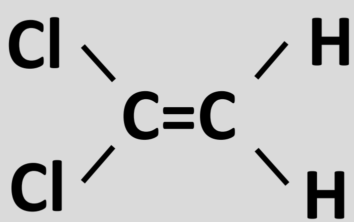
Perchloroethene (PCE)



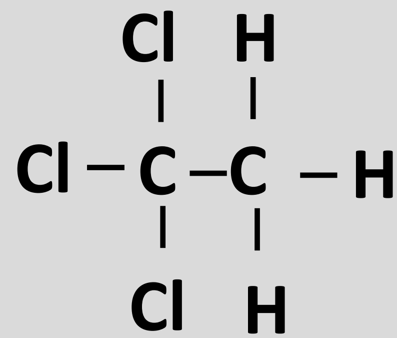
Trichloroethene (TCE)



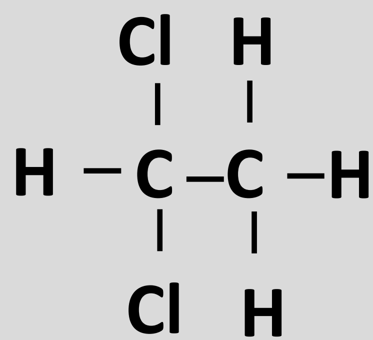
1,1-Dichloroethene (DCE)



1,1,1-Trichloroethane (TCA)



1,1-Dichloroethane (DCA)



Natural Attenuation of Chlorinated Solvents

<u>Abiotic Degradation:</u>

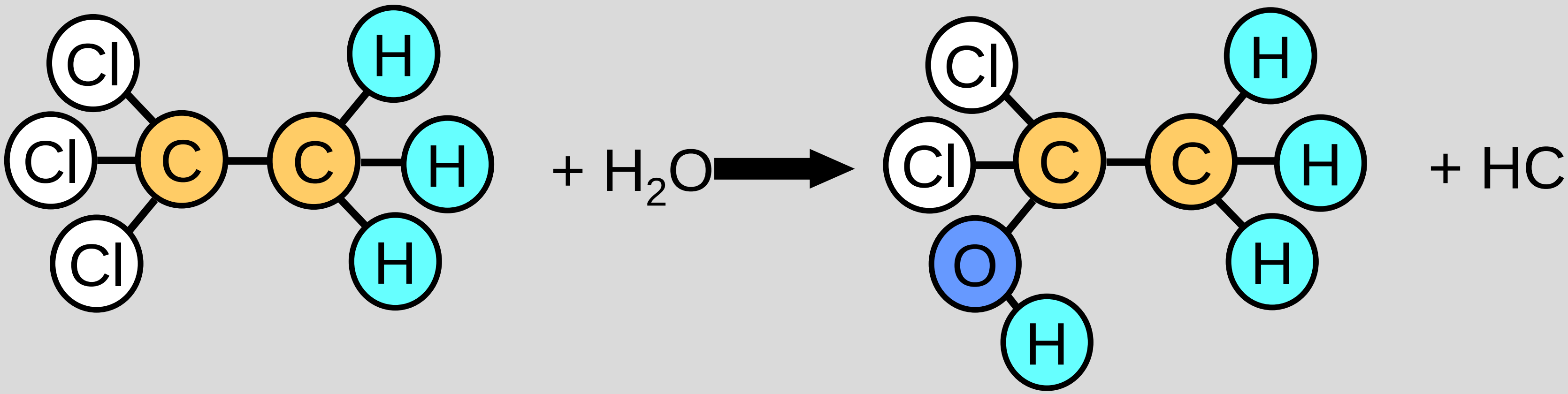
- Hydrolysis
- Dehydrohalogenation
- Reaction with reduced Iron (e.g. FeS)

<u>Biotic Degradation:</u>

- Aerobic
- Anaerobic

Abiotic Degradation: Hydrolysis

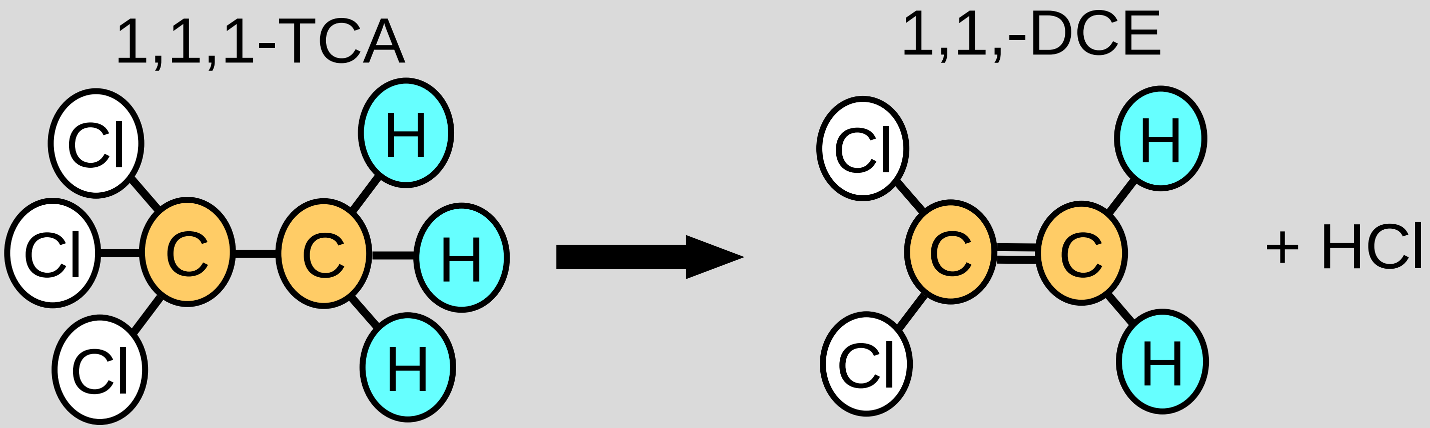
1,1,1-TCA



More Chlorine
-slower hydrolysis
-half-life: 100 - 1000 years

Less Chlorine
-faster hydrolysis
half-life: days- months

Abiotic Degradation: Dehydrohalogenation



More Chlorine
-Faster RXN rate

Less Chlorine
-Slower RXN rate

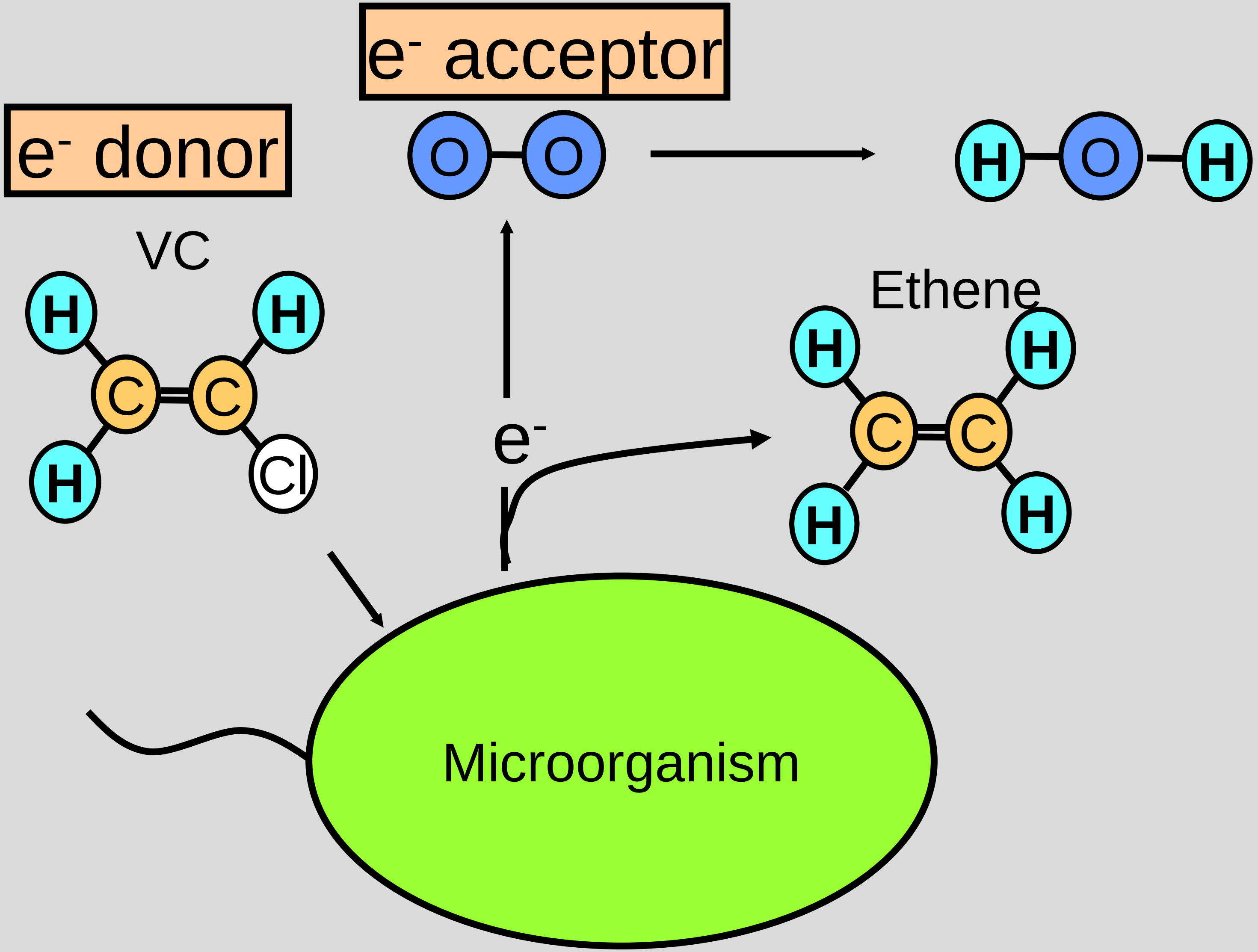
Chlorinated Solvent Biodegradation

Process	Electron Donor	Electron Acceptor
Halorespiration	Hydrogen	Chlorinated solvent
Aerobic Oxidation	Chlorinated solvent	Oxygen
Anaerobic Oxidation	Chlorinated solvent	Fe(III), CO_2
Aerobic Cometabolism	other organic compound	Oxygen
Anaerobic Cometabolism	other organic compound	NO_2, Fe(III), SO_4, CO_2

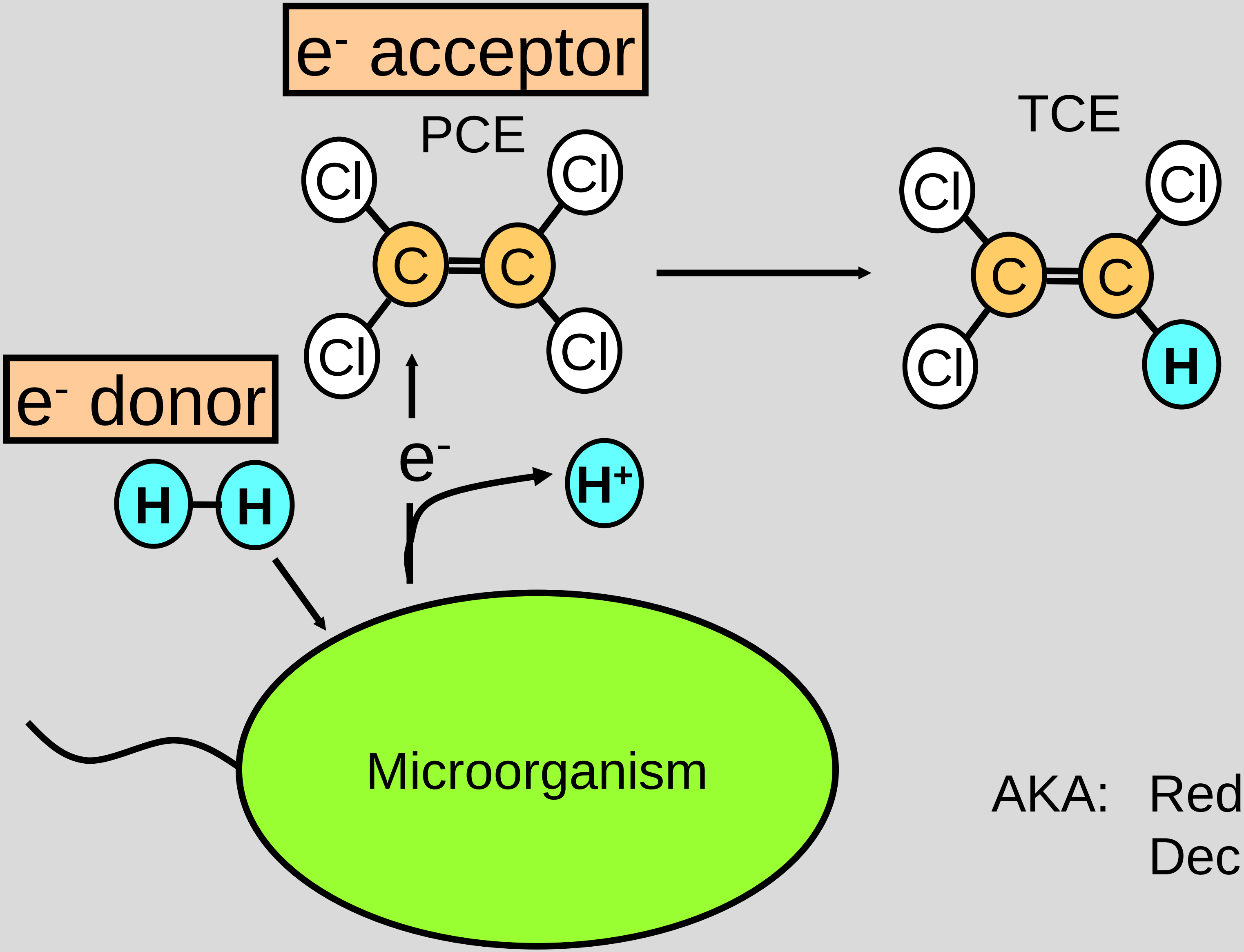
Other organic compound could be:

- non-chlorinated organic contaminant
- organic carbon added to facilitate halorespiration (e.g., methanol)

Biodegradation: Aerobic Respiration



Biodegradation: halorespiration

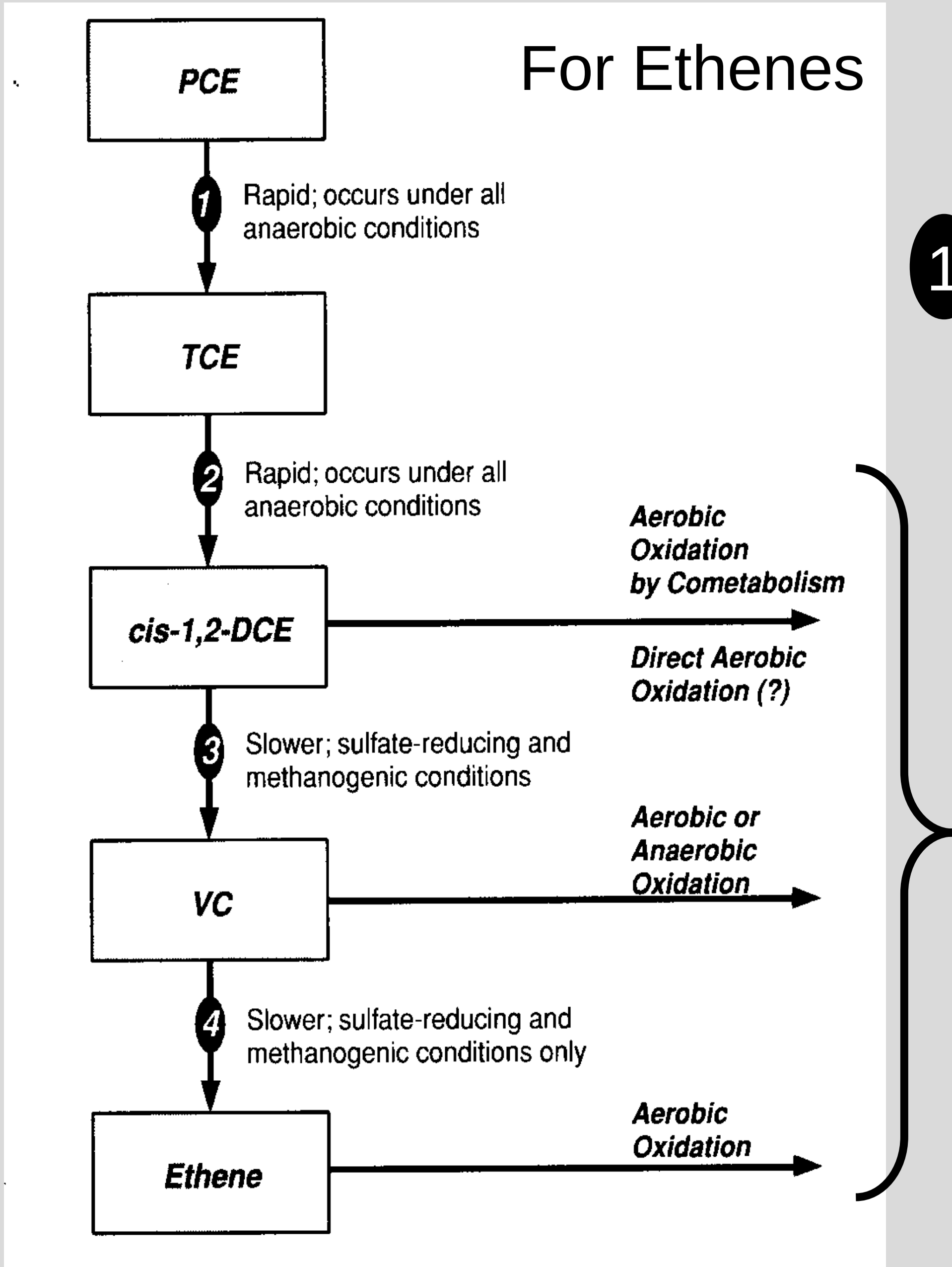


AKA: Reductive
Dechlorination

Biodegradation Processes for Chlorinated Solvents

Compound	Halo-respiration	Aerobic Oxidation	Anaerobic Oxidation	Aerobic Cometabolism	Anaerobic Cometabolism
PCE	X				X
TCE	X			X	X
DCE	X	X	X	X	X
Vinyl Chloride	X	X	X	X	X
1,1,1-TCA	X			X	X
1,2,-DCA	X	X		X	X
Chloroethane		X		X	
Carbon Tetrachloride	X				X
Chloroform	X			X	X
Dichloromethane	X	X	X	X	

Halorespiration vs. Other Degradation Processes



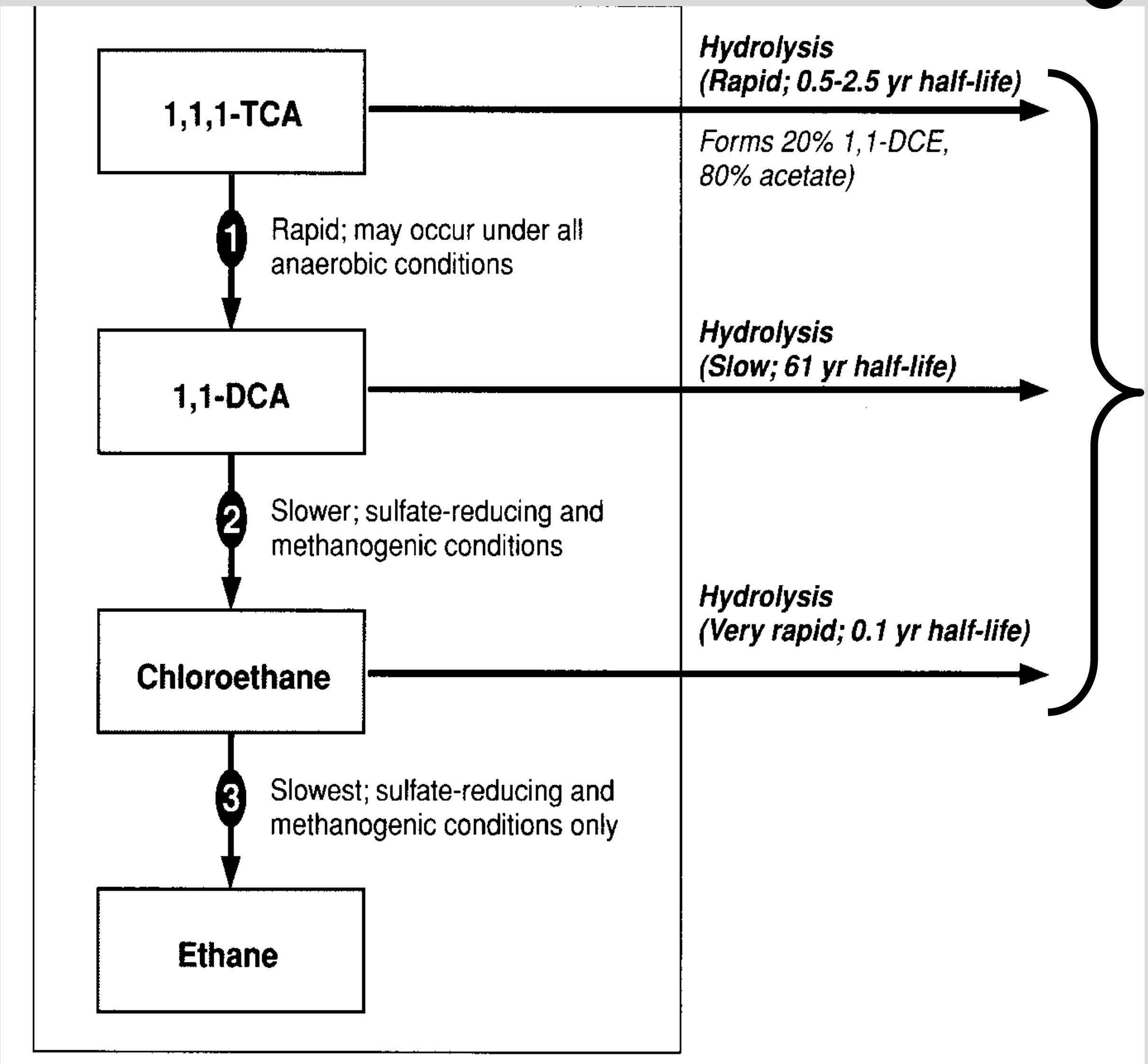
1 = step in halorespiration process

Alternative Degradation Mechanisms

Halorespiration vs. Other Degradation Processes

For Ethanes

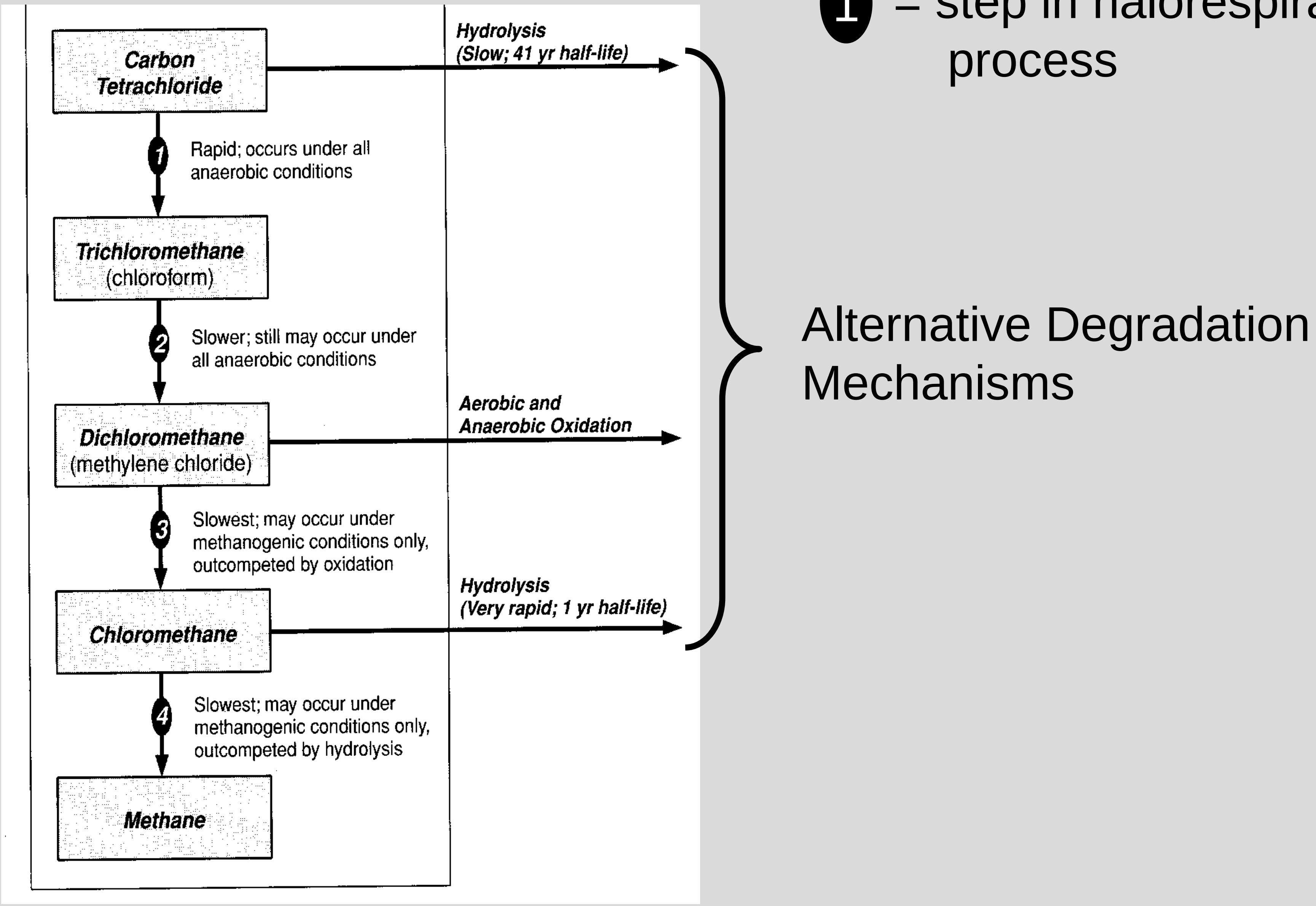
1 = step in halorespiration process



Alternative Degradation Mechanisms

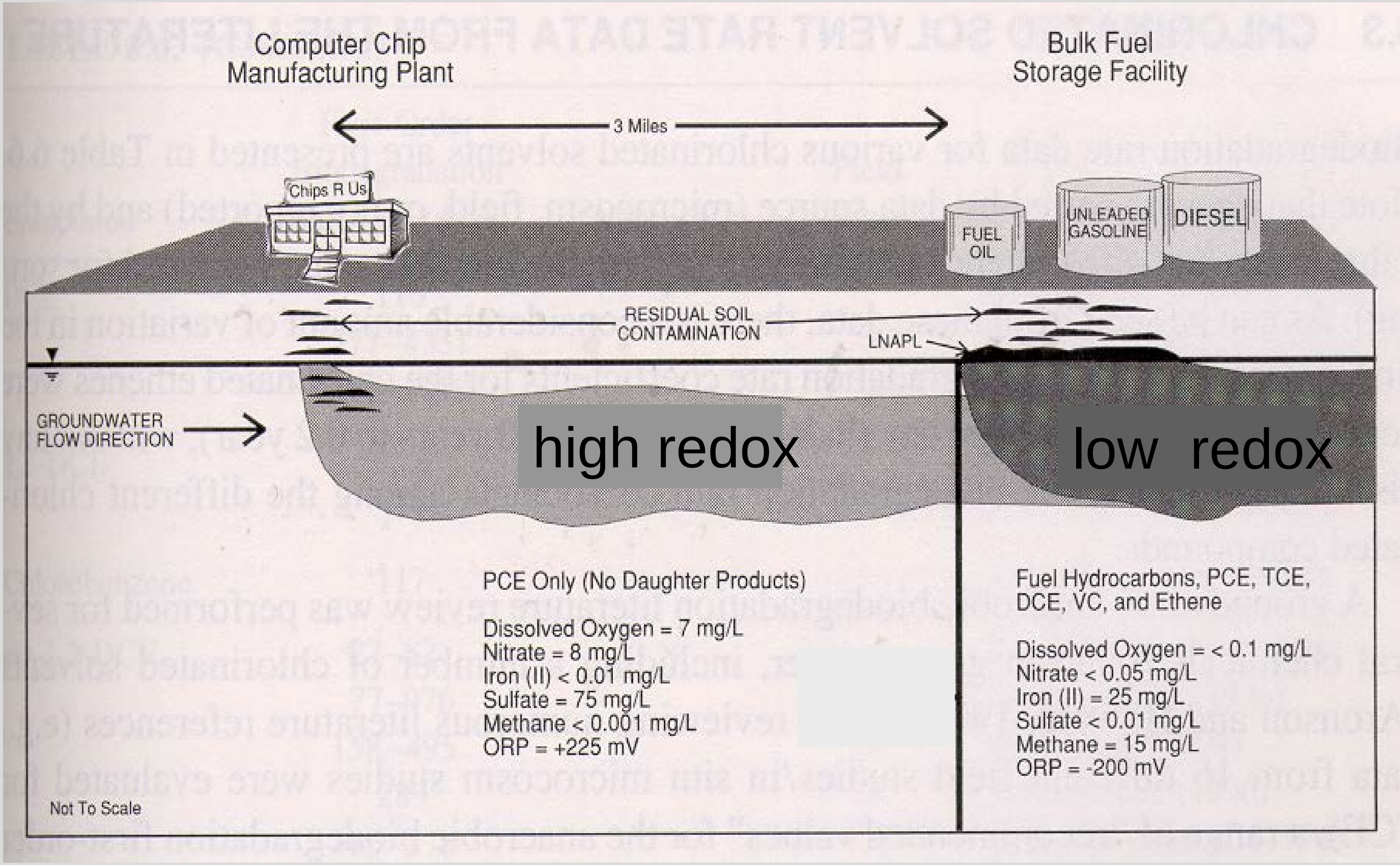
Halorespiration vs. Other Degradation Processes

For Methanes

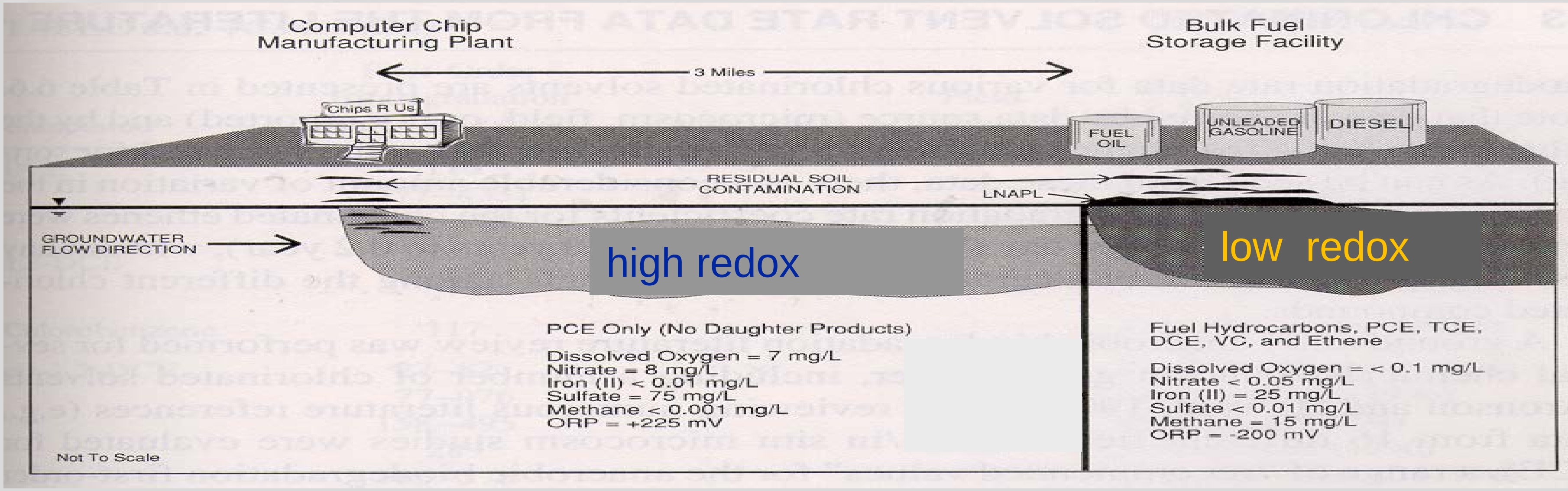


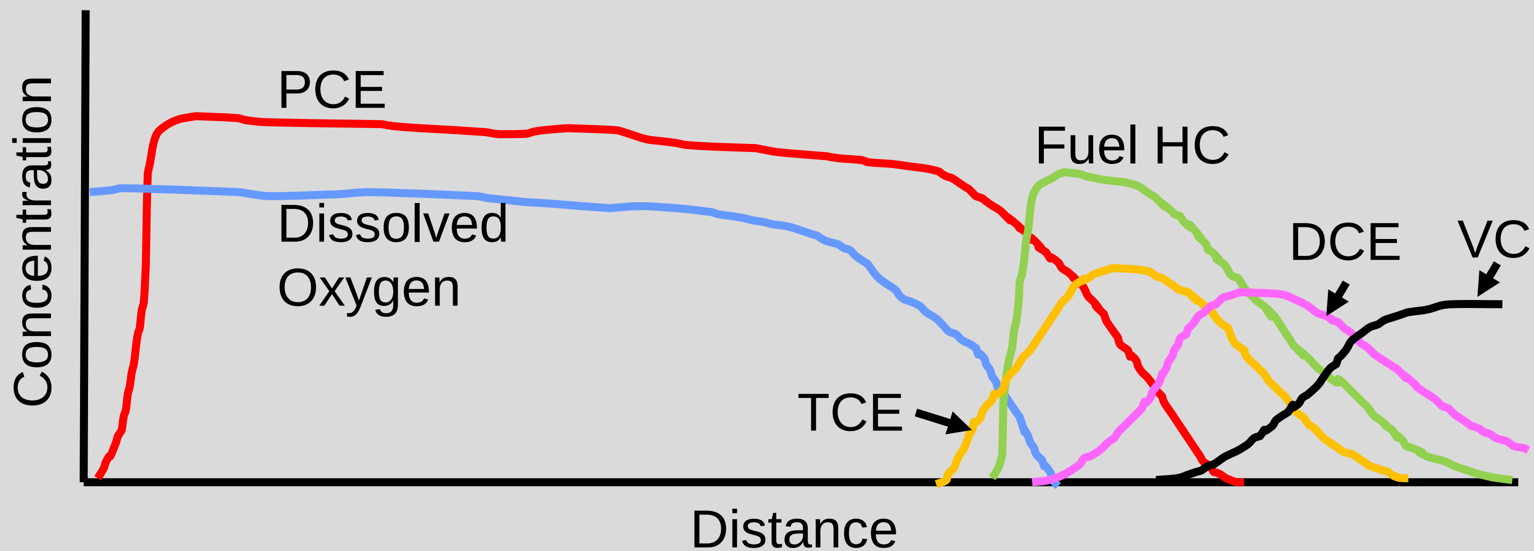
1 = step in halorespiration process

Solvent Plume Characteristics Change with Redox



Solvent Plume Characteristics Change with Redox





Chlorinated Solvent Degradation

- Biodegradation initiated by halorespiration (reductive dechlorination)
- Rates are faster for more highly chlorinated compounds
- Dehydrohalogenation, reaction with reduced Fe are major abiotic mechanisms for degradation

Data Supporting Natural Attenuation

- Presence of daughter products (DCE, VC, Ethene)
- Concurrent attenuation of BTEX
- Abundance of chloride
- High Alkalinity in plume area