Contaminant Fate and Transport Processes

Amended by Fuentes After P. B. Bedient

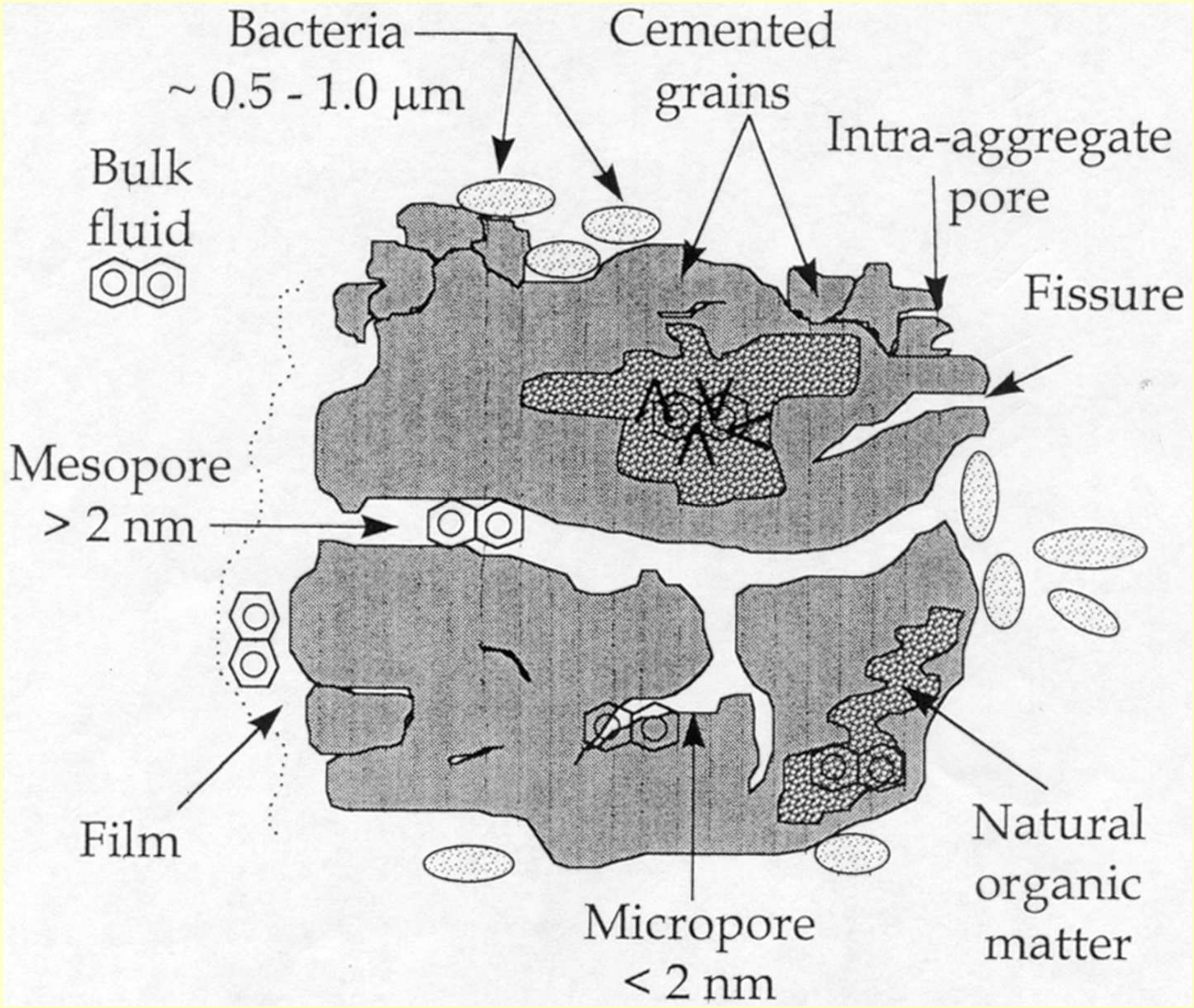
Fate and Transport

- Advection and Hydrodynamic Dispersion
- Chemical (abiotic) processes
- Biodegradation (biotic processes)
- Sorption and Retardation (inter-phase transfer)
- Volatilization (inter-phase transfer)

Sorption and Retardation

- Sorption – association of dissolved or gaseous contaminant with a solid material
- Adsorption – surface process
- Absorption – internal process
- Leads to retardation of the contaminant front
- Desorption – reverse of either sorption process

Soil Grain Sorption

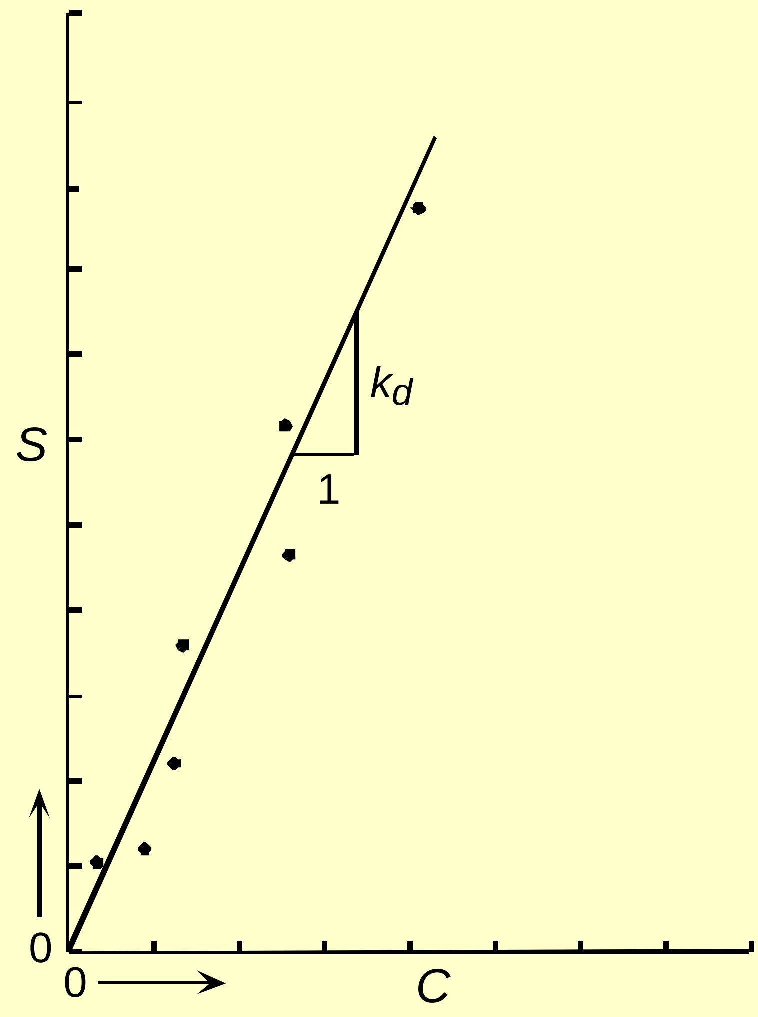


Linear Sorption Isotherm

Sorption linearly related to aqueous concentration.

Partition coefficient is K_d

K_d is related to K_{ow}



Partitioning to Solid Phase

- Octanol water partition coefficient

$$k_{ow} = \frac{[A]_{\text{octanol}}}{[A]_{\text{water}}}$$

- Distribution coefficient

$$k_d = \frac{[A]_{\text{solid}}}{[A]_{\text{aqueous}}}$$

- Fraction in aqueous phase

$$f_w = \frac{1}{1 + \left(\frac{1}{n} - 1\right) k_d}$$

Regression Eqns for Sorption

Equation (a)	No. (b)	r^2 (c)	Chemical Class Represented	Ref.
$\log k_{oc} = -0.55 \log S + 3.64$ (S in mg/L)	106	0.71	Wide variety, mostly pesticides	Kenaga et al., (1978)
$\log k_{oc} = -0.54 \log S + 0.44$ (S in mole fraction)	10	0.94	Mostly aromatic or polynuclear aromatics; two chlorinated	Karickhoff et al., (1979)
$\log k_{oc} = -0.557 \log S + 4.277$ (S in µ moles/L)	15	0.99	Chlorinated hydrocarbons	Chiou et al., (1979)
$\log k_{oc} = 0.544 \log k_{ow} + 1.377$	45	0.74	Wide variety, mostly pesticides	Kenaga et al, (1978)
$\log k_{oc} = 0.937 \log k_{ow} - 0.006$	19	0.95	Aromatics, polynuclear aromatics, triazines and dinitroaniline herbicides	Brown et al. (1981)

Retardation Factor

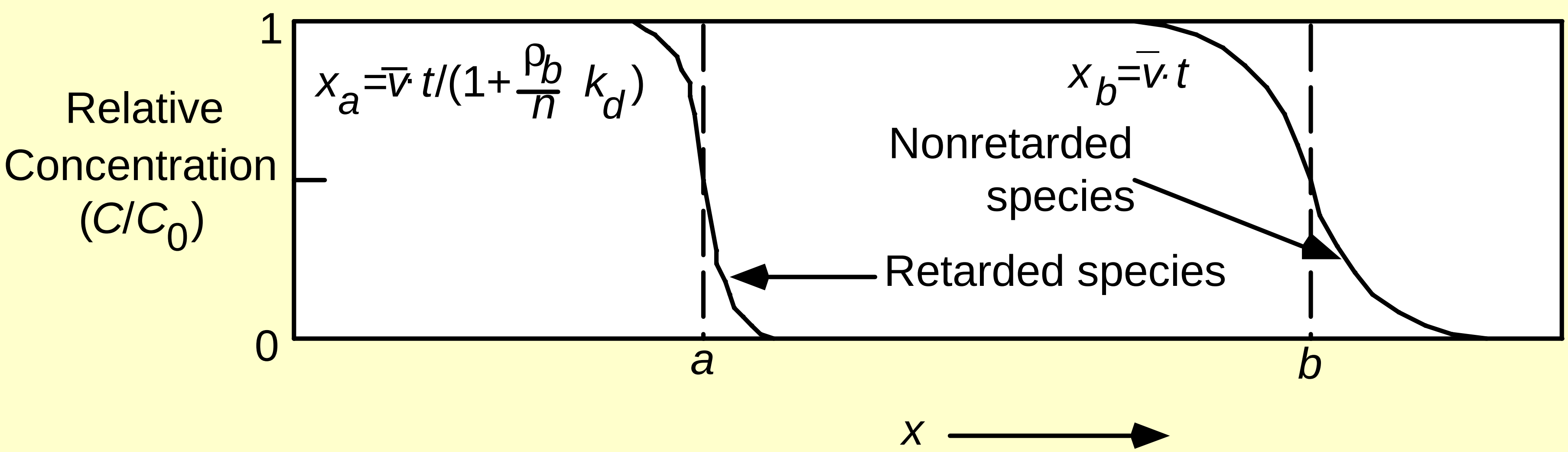
$$D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{\rho_b}{n}\frac{dS}{dt} = \frac{\partial C}{\partial t}$$

$$R\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x}$$

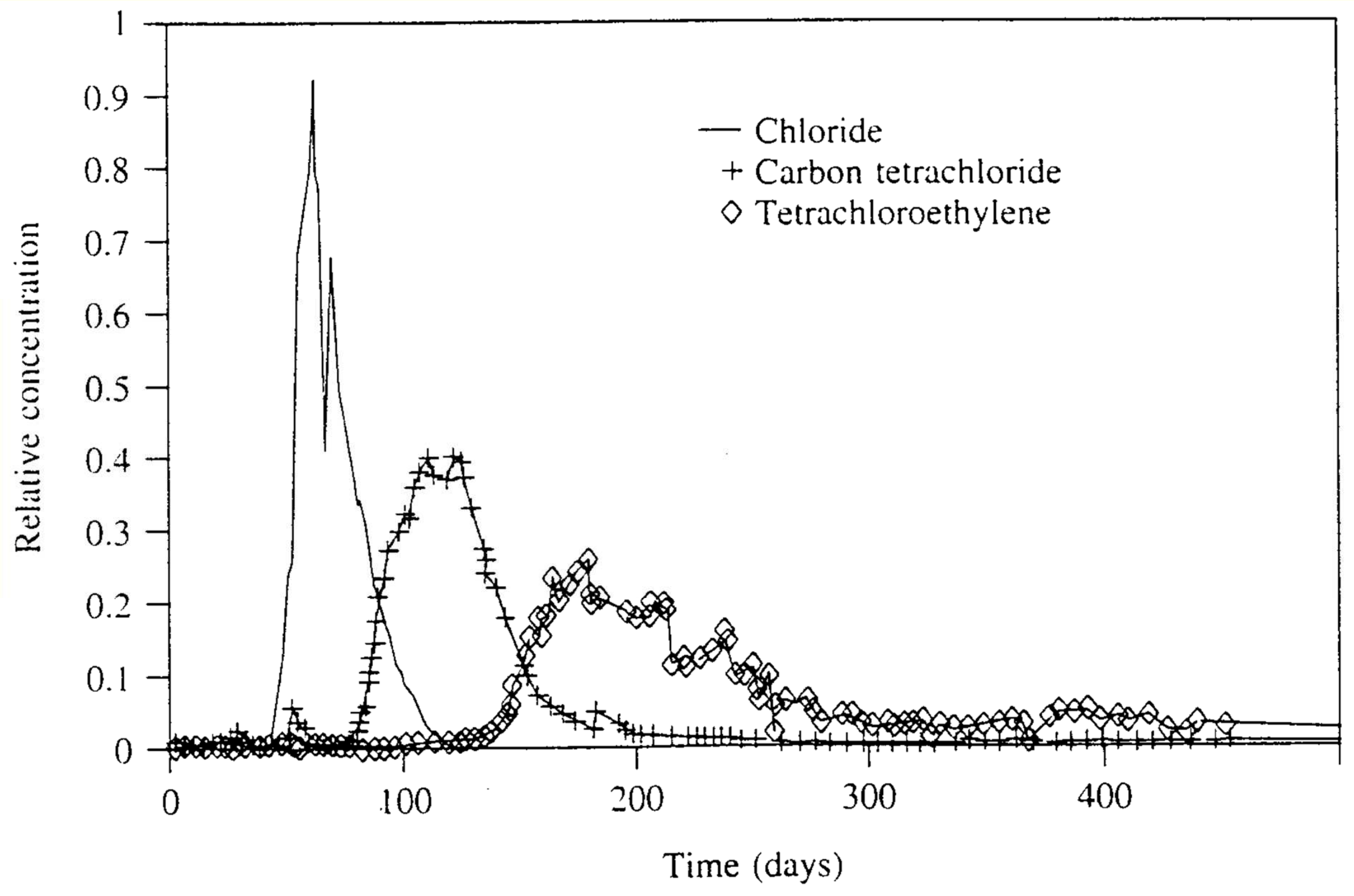
$$R = \left(1 + \frac{\rho_b}{n} k_d\right)$$

Retarded versus Non-retarded Species

- Sorption slows rate of advance of front
- Sorbing fronts will eventually get there
- Some compounds irreversibly sorb to soil

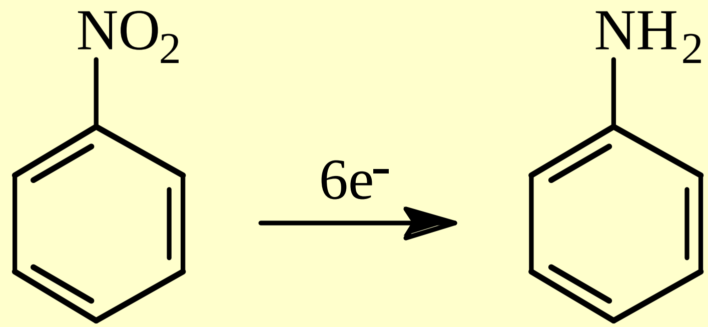


Retardation of Tracers



Abiotic Fate Processes

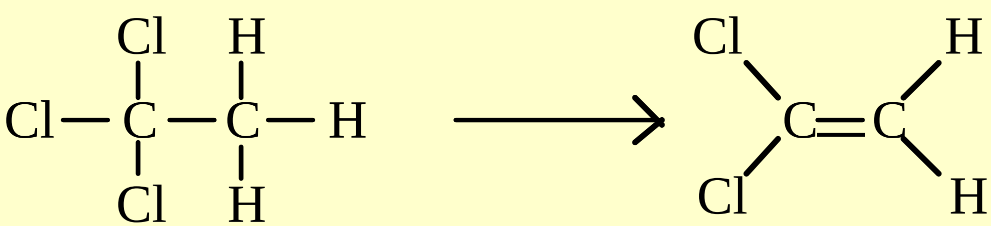
- Hydrolysis
- Oxidation-Reduction
- Elimination



nitrobenzene analine

$$CH_3CH_2Cl \xrightarrow{2e^-} CH_3CH_3 + Cl^-$$

chloroethane ethane + chloride



Compound/ Family	Formula	Specific Gravity	Solubility (mg/L)	K_{ow}	Vapor Pressure (mm Hg)	Henry's Law (unitless)
			Fuels and derivatives			
Benzene	C_6H_6	0.879	1750	130	60	0.22
Toluene	$C_6H_5CH_3$	0.866	535	130	22	0.26
Ethylbenzene	C_8H_{10}	0.867	152	1400	7	0.32
Phenol	C_6H_6O	1.071	93,000	29	0.2	1.89×10^{-5}
			Ketones			
Acetone	CH_3COCH_3	0.791	inf	0.6	89	0.00104
Methyl ethyl ketone	$CH_3COCH_2CH_3$	0.805	2.68×10^5	1.8	77.5	0.00181
			Halogenated aliphatics			
Tetrachloroethene	CCl_2CCl_2	1.631	150	390	14	1.21
Trichloroethene	C_2HCl_3	1.466	1100	240	60	0.42
cis-1,2-Dichloroethene	$C_2H_2Cl_2$	1.27	3500	5	206	1.33
Vinyl chloride	CH_2CHCl	0.908	2670	24	266	3.58

Volatilization

- Transfer of contaminant from aqueous phase, NAPL, or sorbed phase directly to gas phase
- Equilibrium partitioning similar to octanol-water partitioning
- Partitioning equation known as Henry's Law
- H_c is the relationship between partial pressure and aqueous concentration of component

$$H_c = \frac{P_c}{[C]_{aq}}$$

- 20% Oxygen (0.2 atm partial pressure) => 8 mg/L D.O.

Biotic Transformations

- Aerobic and anaerobic biodegradation
- Reduces aqueous concentrations of contaminant
- Reduction of contaminant mass
- Most significant process resulting in reduction of contaminant mass in a system

Biodegradation Processes

- Conversion of contaminants to mineralized (e.g. CO_2, H_2O, and salts) end-products via biological mechanisms
- Biotransformation refers to a biological process where the end-products are not minerals (e.g., transforming TCE to DCE)
- Involves the process of extracting energy from organic chemicals via oxidation of the organic chemicals

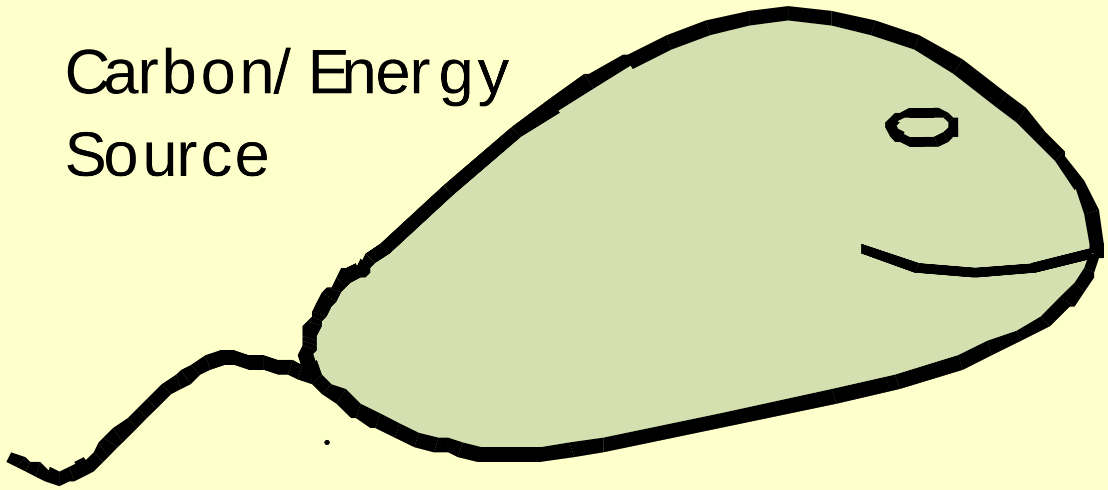
Fundamentals of Biodegradation

- All organics are biodegradable, BUT biodegradation requires specific conditions
- There is no Superbug - not Volkswagon
- Contaminants must be bioavailable
- Biodegradation rate and extent is controlled by a “limiting factor”

Requirements for Microbial Growth

Electron Acceptor
(O_2, NO_3^-, SO_4^{2-}, etc.)

Carbon/Energy
Source

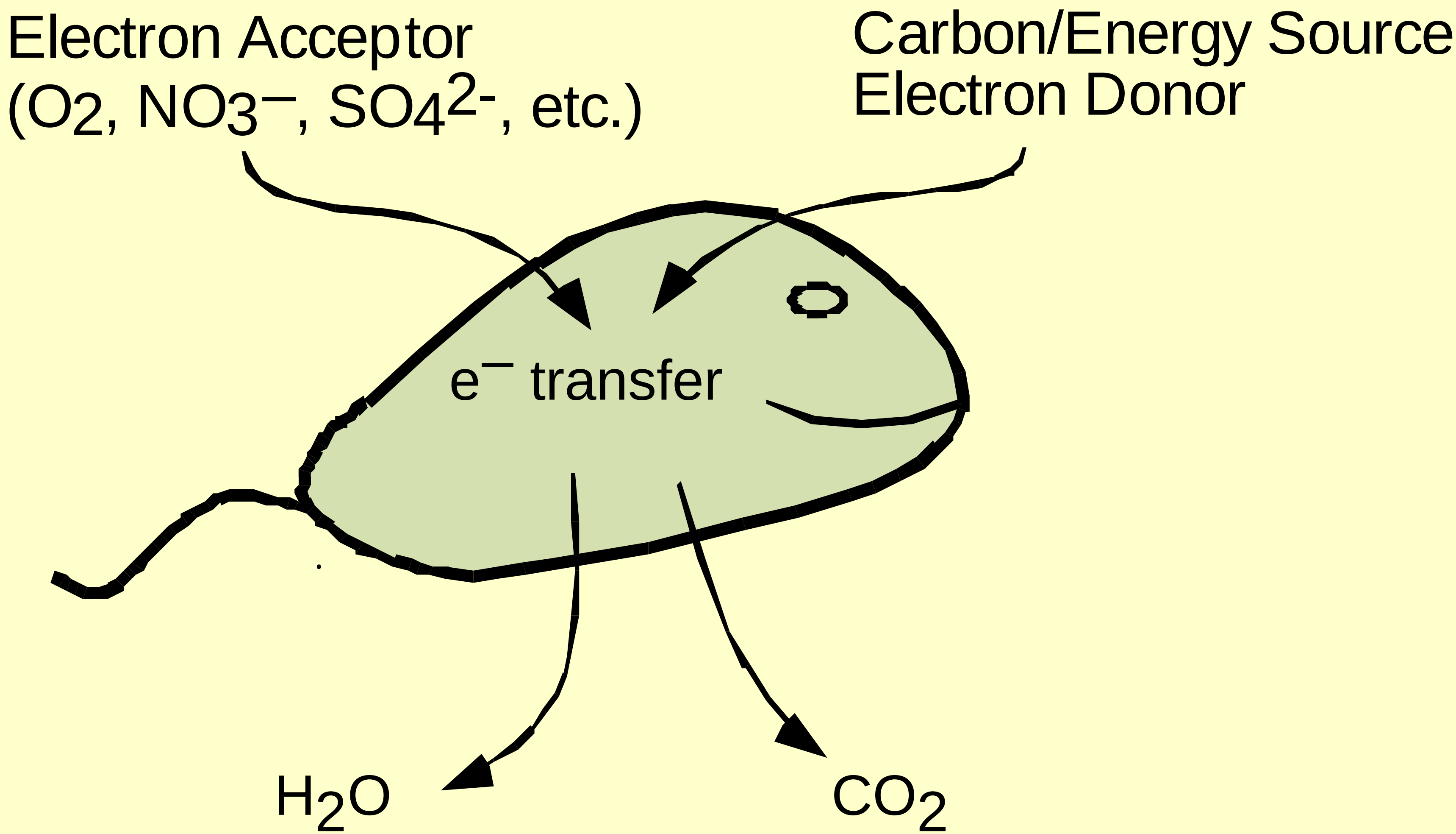


Environmental
Conditions
(Temp, pH, Eh)

Nutrients (N, P)

Trace Elements

Electron Exchange



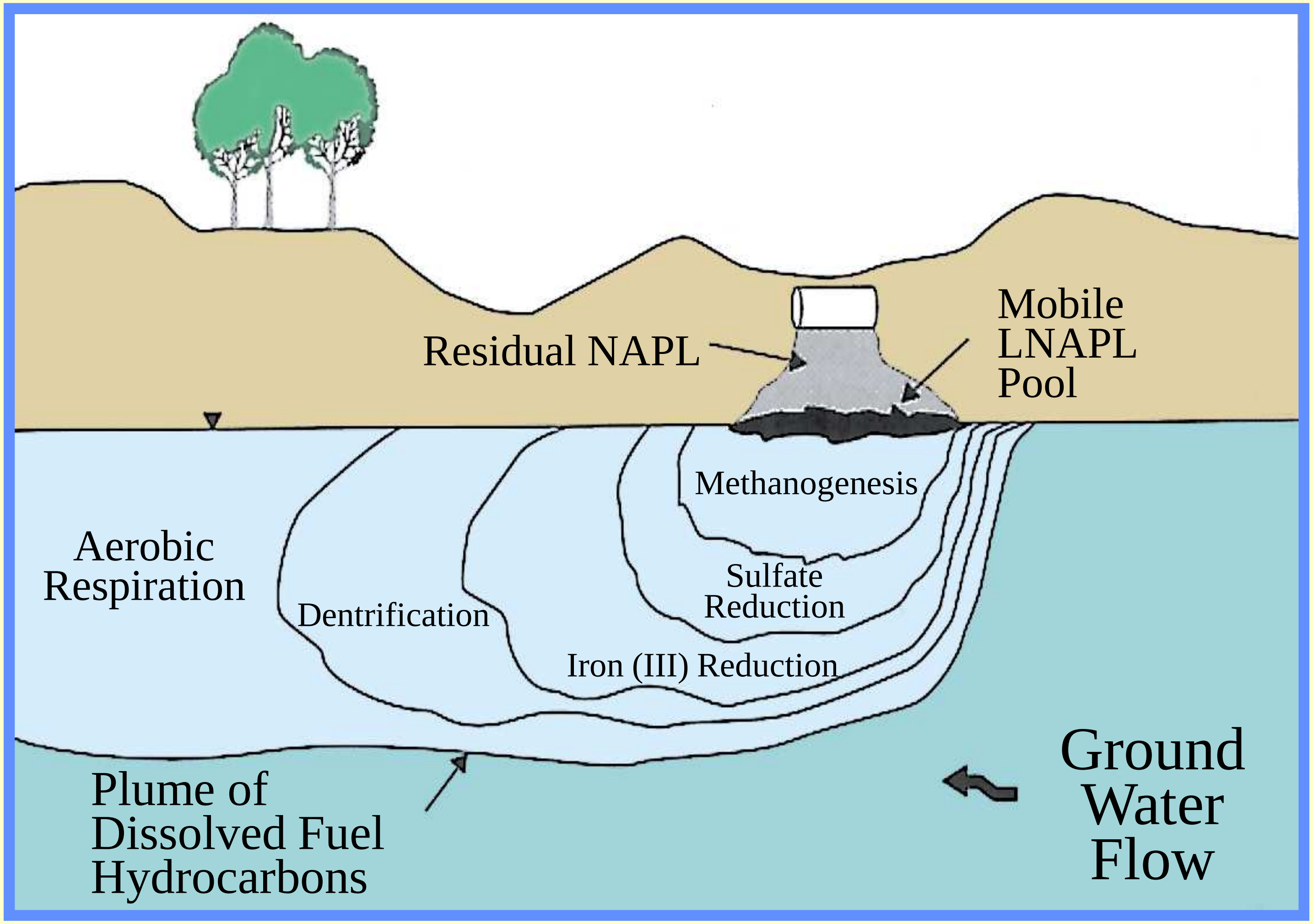
Aerobic vs. Anaerobic

- If oxygen is the terminal electron acceptor, the process is called aerobic biodegradation
- All other biological degradation processes are classified as anaerobic biodegradation
- In most cases, bacteria can only use one terminal electron acceptor
- Facultative aerobes use oxygen, but can switch to nitrate in the absence of oxygen

Bacterial Metabolism

Aerobic	Anaerobic
Oxidation	Denitrification
Cometabolism	Manganese reduction
	Iron reduction
	Sulfate reduction
	Methanogenesis

Electron Acceptor Zone Formation



(Source: W,R, N, & W, 1999.) **(Adapted from Lovley et al., 1994b.)**

Dependence on Redox Condition

Compound(s)	Aerobic	Anaerobic
Acetone	1	1
BTEX	1	2 to 4
PAH's	1	3 to 4
PCB's		
highly substituted	4	2
minimally substituted	2	4
Chlorinated ethenes		
PCE	4	1 to 2
TCE	3	1 to 2
DCEs	3	2 to 3
Vinyl chloride	1 to 2	3 to 4

1 Highly biodegradable
2 Moderately biodegradable
3 Slow biodegradation
4 Not biodegraded

Substrates

- Primary substrate – Cake
  - enough available to be the sole energy source
- Secondary substrate – Icing
  - provides energy, not available in high enough concentration
- Cometabolism – Sprinkles
  - fortuitous transformation of a compound by a microbe relying on some other primary substrate

Transformation Process

Acetone	×			
BTEX	×			
PAHs	×	×		
PCBs				
highly substituted			×	
minimally substituted	×			
Chlorinated ethenes				
PCE			×	×
TCE			×	×
DCEs			×	×
Vinyl Chloride	×		×	×

Stoichiometry

- Electron Donor to Electron acceptor ratios
  - Hydrocarbon requirements for electron acceptor are well defined
  - Electron donor requirements for dechlorination are poorly defined
  - Cometabolic processes are not predictable
- Each Electron Donor/Electron Acceptor pair has a unique stoichiometric ratio

Oxygen Utilization of Substrates

- Benzene: $C_6H_6 + 7.5O_2 \longrightarrow 6CO_2 + 3H_2O$
- Stoichiometric ratio (F) of oxygen to benzene

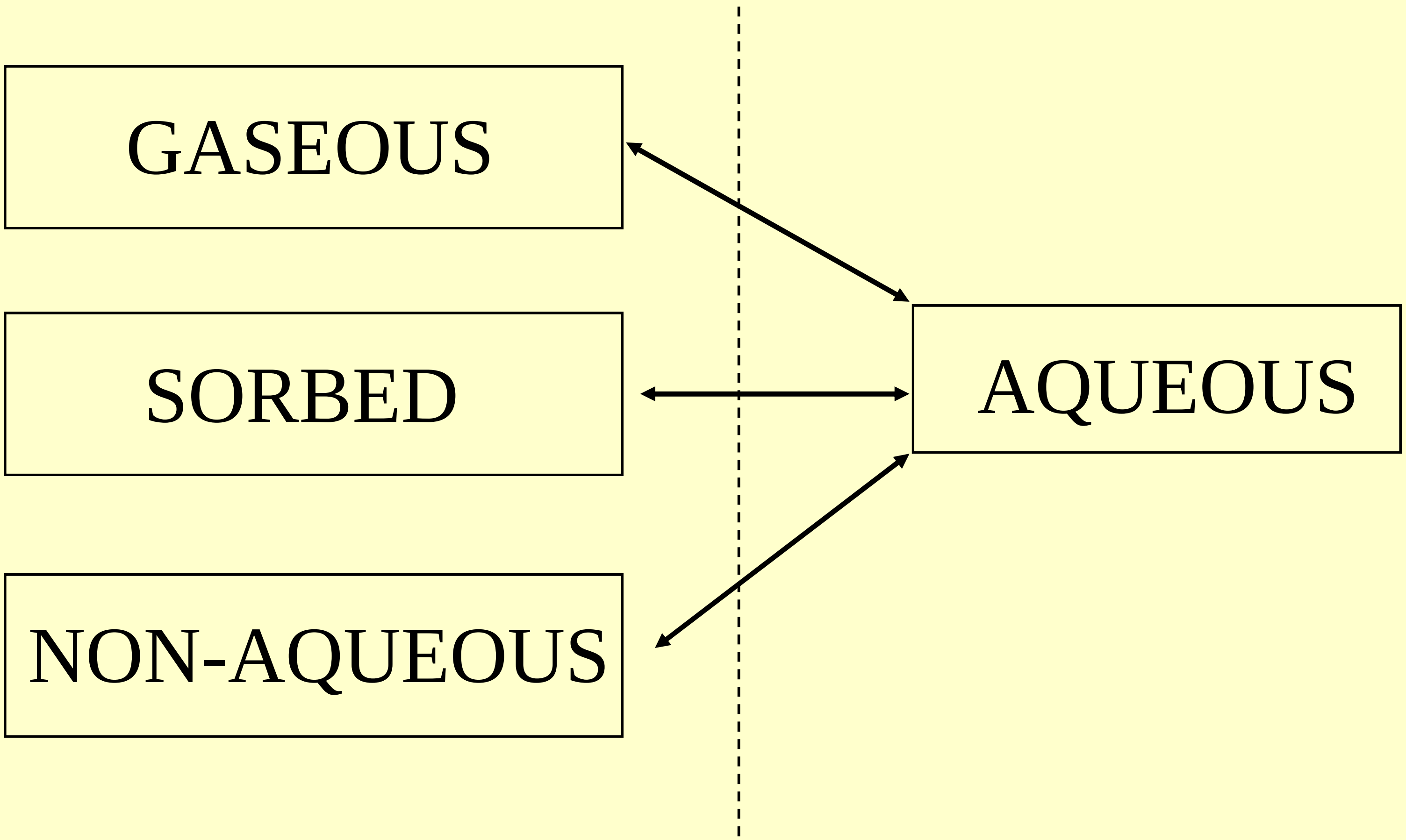
$$F = \frac{7.5\ \text{molO}_2}{1\ \text{molC}_6\text{H}_6}\frac{32\ \text{mgO}_2}{1\ \text{molO}_2}\frac{1\ \text{molC}_6\text{H}_6}{(12 \bullet 6 + 1 \bullet 6)\ \text{mgC}_6\text{H}_6}$$

$$F = 3.07\ \text{mgO}_2/\text{mgC}_6\text{H}_6$$

- Each mg/L of benzene consumes 3.07 mg/L of O_2

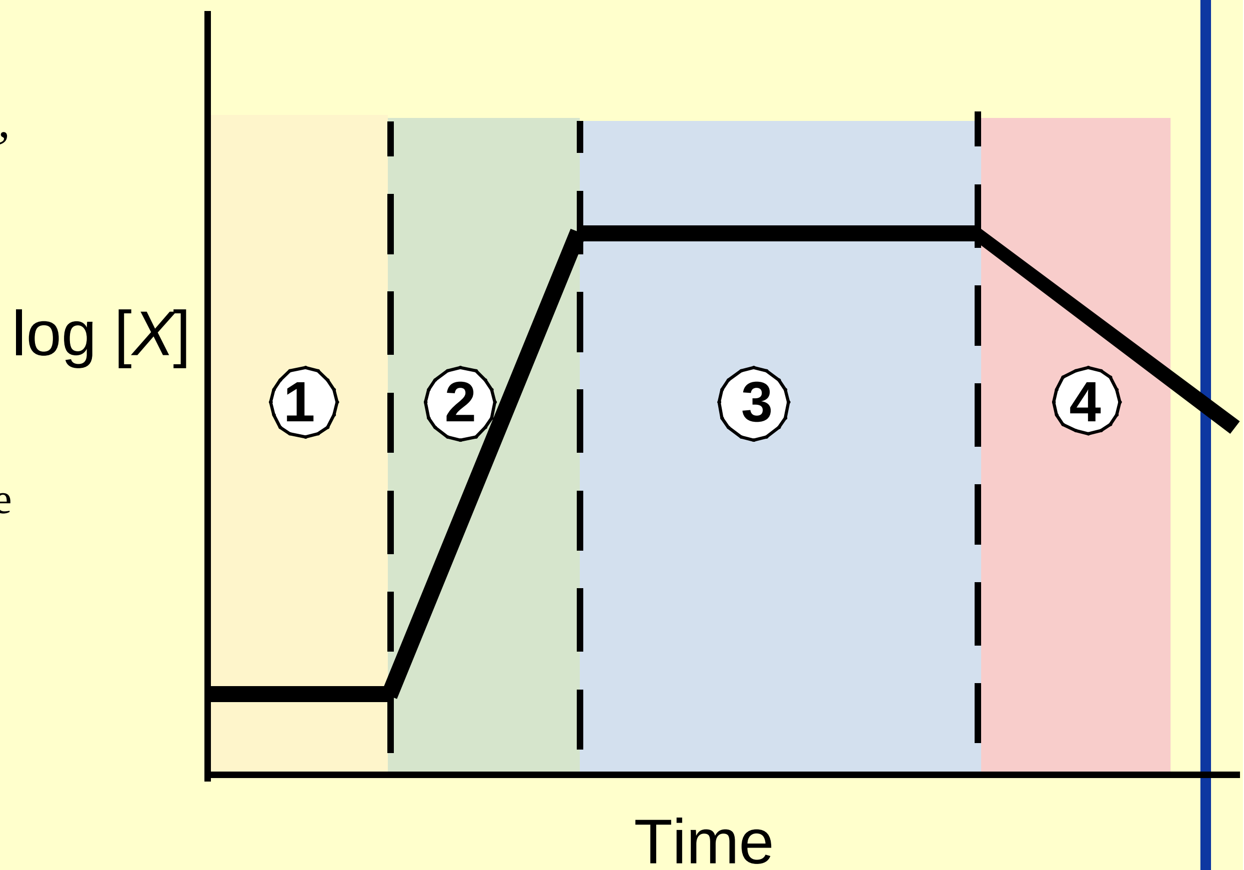
Bioavailability

Not accessible | Accessible



Microbial Growth

- **Region 1:**
  Lag phase
  - microbes are adjusting to the new substrate (food source)
- **Region 2**
  Exponential growth phase,
  - microbes have acclimated to the conditions
- **Region 3**
  Stationary phase,
  - limiting substrate or electron acceptor limits the growth rate
- **Region 4**
  Decay phase,
  - substrate supply has been exhausted



Biodegradation Kinetics

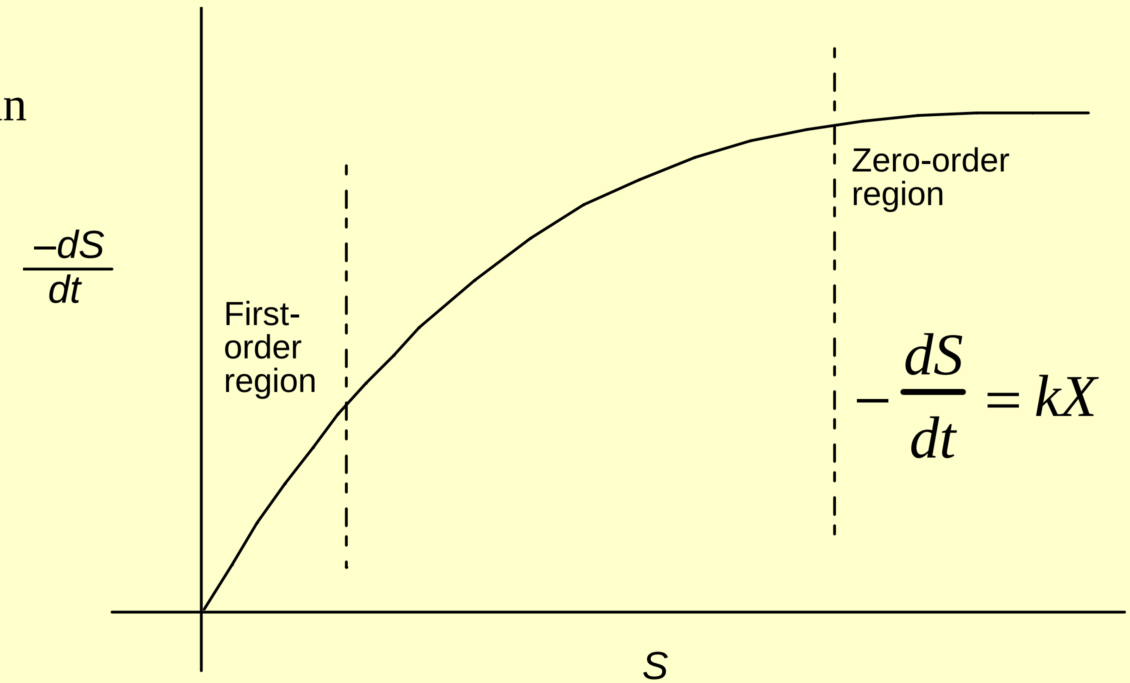
- The rate of biodegradation or biotransformation is generally the focus of environmental studies
- Microbial growth and substrate consumption rates have often been described using ‘Monod kinetics’

$$-\frac{dS}{dt} = \frac{kSX}{K_s + S}$$

- S is the substrate concentration [mg/L]
- X is the biomass concentration [mg/ L]
- k is the maximum substrate utilization rate [sec^{-1}]
- K_S is the half-saturation coefficient [mg/L]

Monod Kinetics

- First-order region, $S << K_S$, the equation can be approximated by exponential decay ($C = C_0 e^{-kt}$)
- Center region, Monod kinetics must be used
- Zero-order region, $S >> K_S$, the equation can be approximated by linear decay ($C = C_0 - kt$)



$$-\frac{dS}{dt} = kX$$

$$-\frac{dS}{dt} = \frac{kSX}{K_s}$$

Modeling Biodegradation

- Three main methods for modeling biodegradation
  - ♦ Monod kinetics
  - ♦ First-order decay
  - ♦ Instantaneous reaction

Modeling First-Order Decay

- $C^{n+1} = C^n e^{-k\Delta t}$
- Generally assumes nothing about limiting substrates or electron acceptors
- Degradation rate is proportional to the concentration
- Generally used as a fitting parameter, encompassing a number of uncertain parameters

- BIOPLUME III can limit first-order decay to the available electron acceptors

Modeling Instantaneous Biodegradation

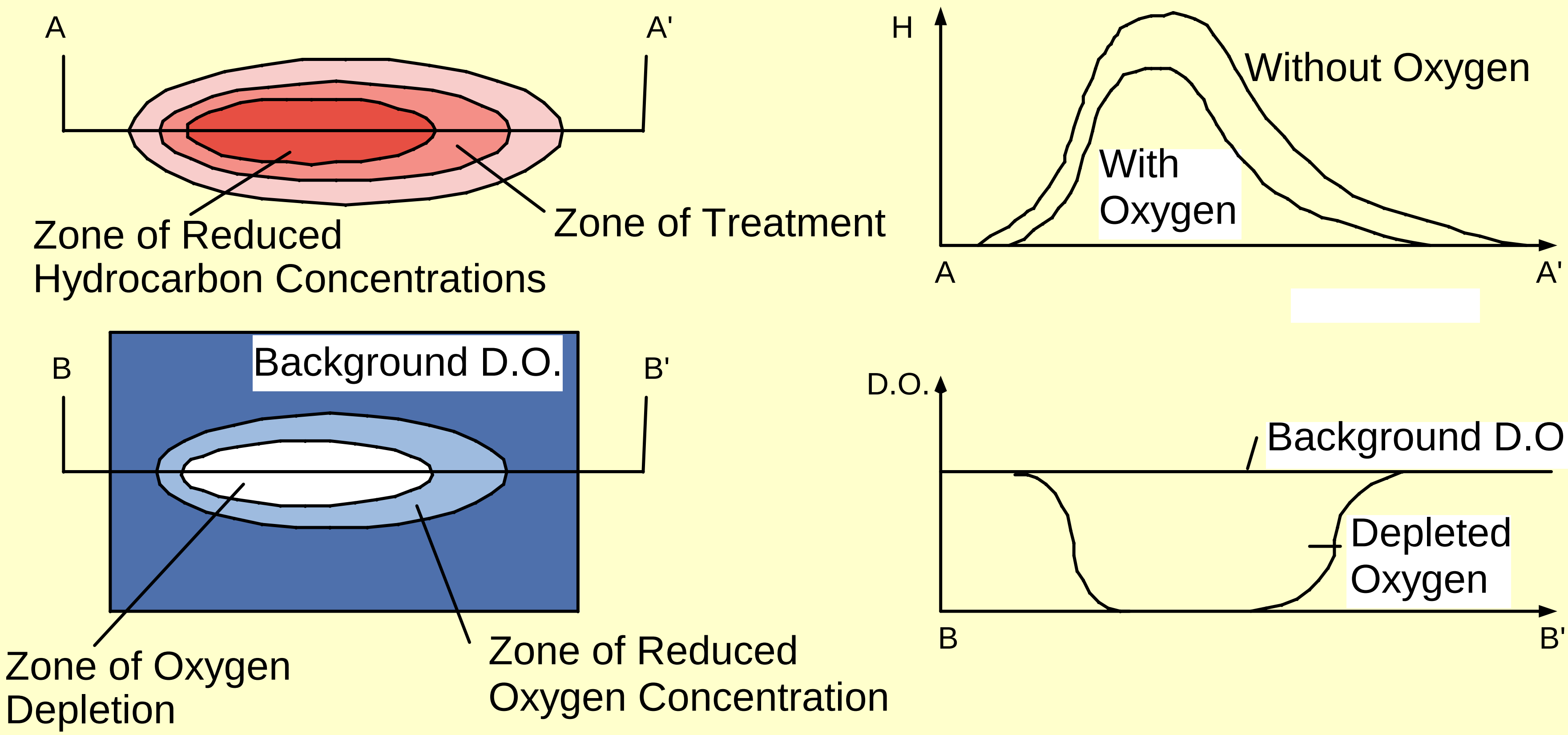
- Excess Hydrocarbon: $H^n > O^n/F$
  - ♦ $O^{n+1} = 0$ $H^{n+1} = H^n - O^n/F$
- Excess Oxygen: $H^n < O^n/F$
  - ♦ $O^{n+1} = O^n - H^nF$ $H^{n+1} = 0$
- All available substrate is biodegraded, limited only by the availability of terminal electron acceptors
- First used in BIOPLUME II

Sequential Electron Acceptor Models

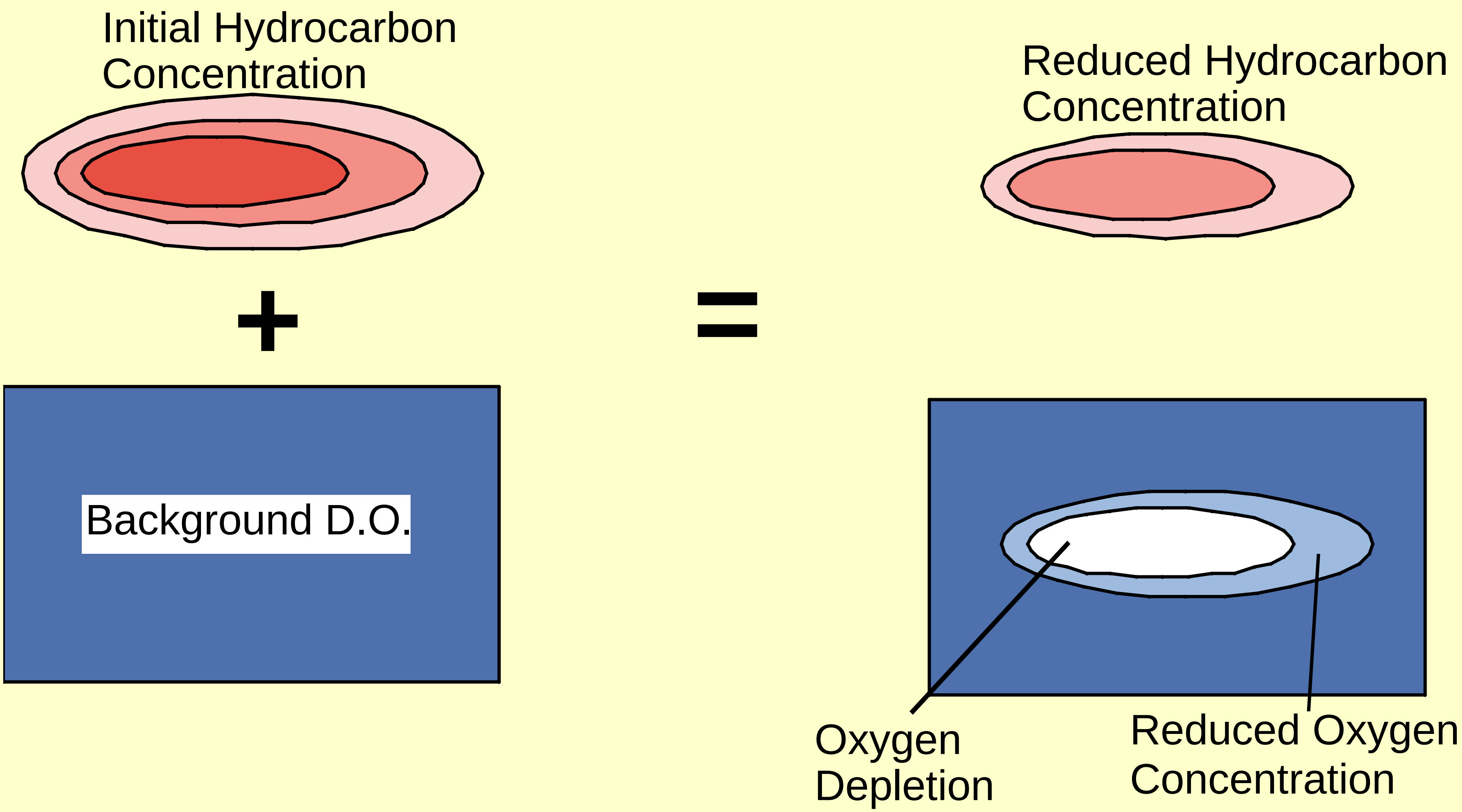
- Newer models, such as BIOPLUME III, RT3D, and SEAM3D allow a sequential process
- After O_2 is depleted, begin using NO_3^-
- Continue down the list in this order

  - O_2 —> NO_3^- —> Fe^{3+} —> SO_4^{2-} —> CO_2

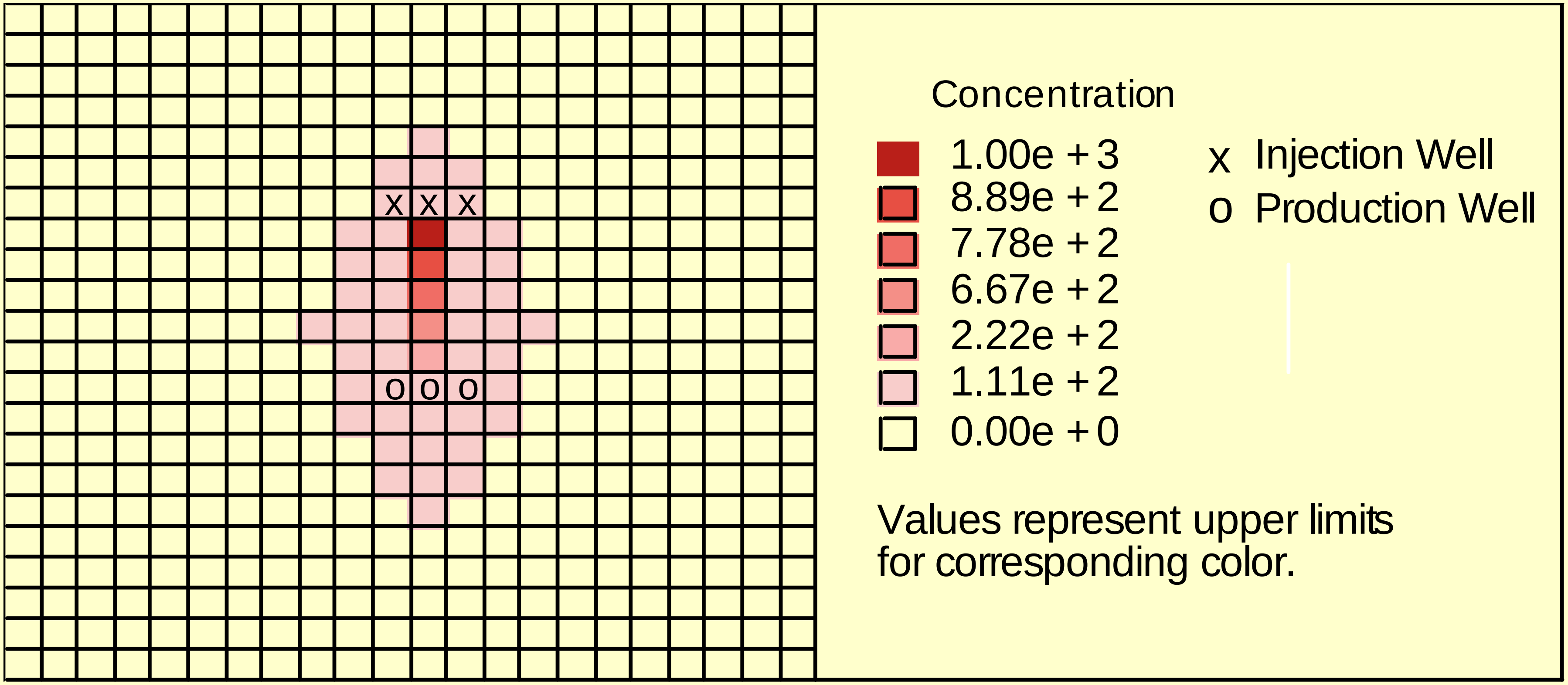
Biodegradation in BIOPLUME II



Principle of Superposition



Initial Contaminant Plume



Model Parameters

Grid Size	20 x 20 cells
Cell Size	50 ft x 50 ft
Transmissivity	0.002 ft^2/sec
Thickness	10 ft
Hydraulic Gradient	.001 ft/ft
Longitudinal Dispersivity	10 ft
Transverse Dispersivity	3 ft
Effective Porosity	0.3

Biodegrading Plume

0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	1	0	0	0	0
0	0	0	1	11	1	0	0	0
0	0	0	6	123	6	0	0	0
0	0	1	38	1000	38	1	0	0
0	0	4	71	831	71	4	0	0
0	0	7	97	710	97	7	0	0
0	1	9	104	600	104	9	1	0
0	0	9	90	449	90	9	0	0
0	0	5	54	285	54	5	0	0
0	0	2	19	109	19	2	0	0
0	0	0	4	24	4	0	0	0
0	0	0	1	4	1	0	0	0
0	0	0	0	1	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0

Original Plume Concentration

0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	1	1	1	1	1	0	0
0	0	2	3	4	3	2	0	0
0	0	3	7	12	8	3	1	0
0	0	4	11	20	13	5	0	0
0	0	2	8	11	8	2	0	0
0	0	0	2	4	2	0	0	0
0	0	0	0	1	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0

Plume after two years

Extraction Only - No Added O_2

Plume Concentrations

0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
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0	0	3	7	15	8	3	0	0
0	0	2	6	10	7	1	0	0
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0	0	0	0	1	0	0	0	0
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0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0

Plume after two years

O_2 Injected at 20 mg/L

0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
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0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0

Plume after two years

O_2 Injected at 40 mg/L

Dehalogenation

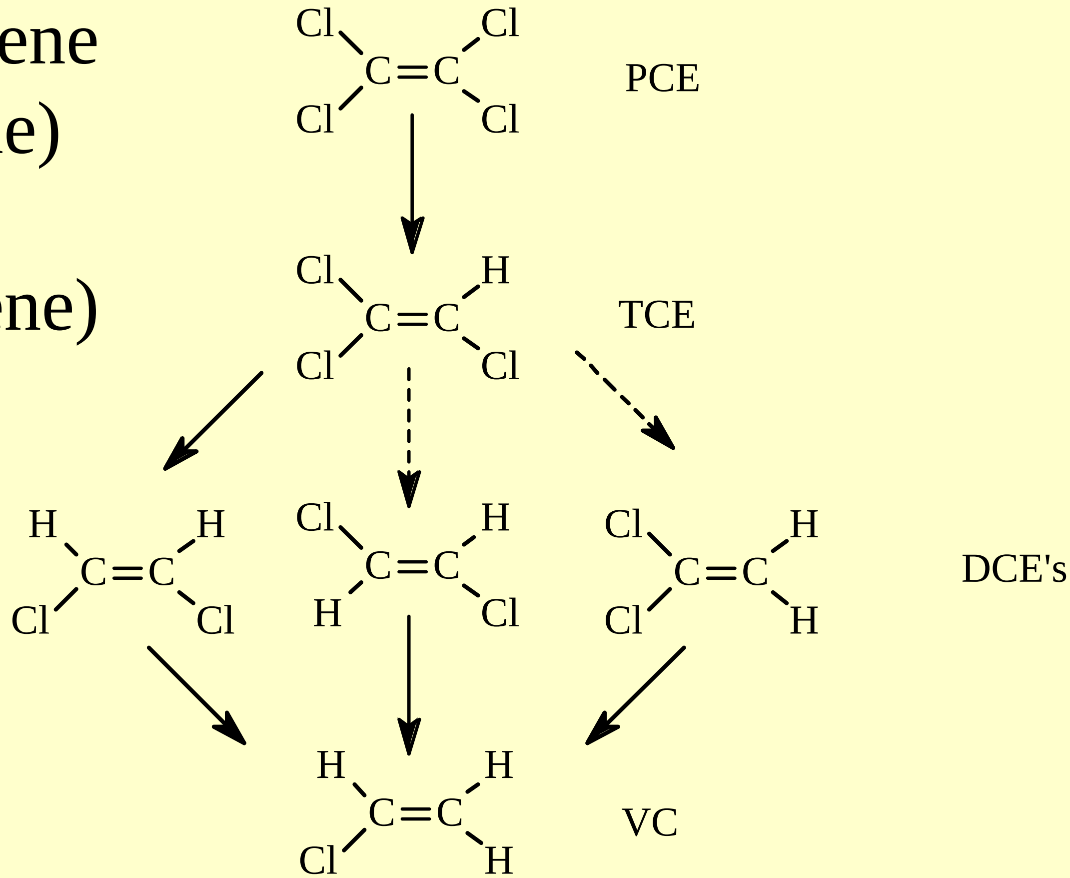
- Dehalogenation refers to the process of stripping halogens (generally Chlorine) from an organic molecule
- Dehalogenation is generally an anaerobic process, and is often referred to as reductive dechlorination

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

- Can occur via dehalorespiration or cometabolism
- Some rare cases show cometabolic dechlorination in an aerobic environment

Dehalogenation of PCE

- PCE (perchloroethylene or tetrachloroethylene)
- TCE (trichloroethylene)
- DCE (cis-, trans-, and 1,1-dichloroethylene
- VC (vinyl chloride)



Biodegradation Models

- Bioscreen
- Biochlor
- BIOPLUME II and III
- RT3D
- MT3D MS
- SEAM 3D