The BIOCHLOR Natural Attenuation Model

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Groundwater Services, Inc.
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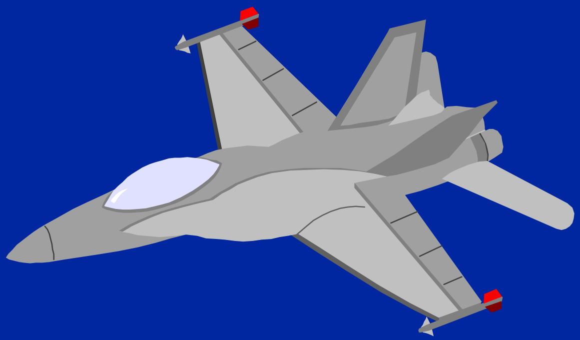


Funded by AFCEE Tech Transfer Division

BIOCHLOR Road Map

- Chlorinated Solvent Biodegradation
- BIOCHLOR "Plume-a-thon" Study
- How BIOCHLOR Works

Chlorinated Solvent Biodegradation Mechanisms

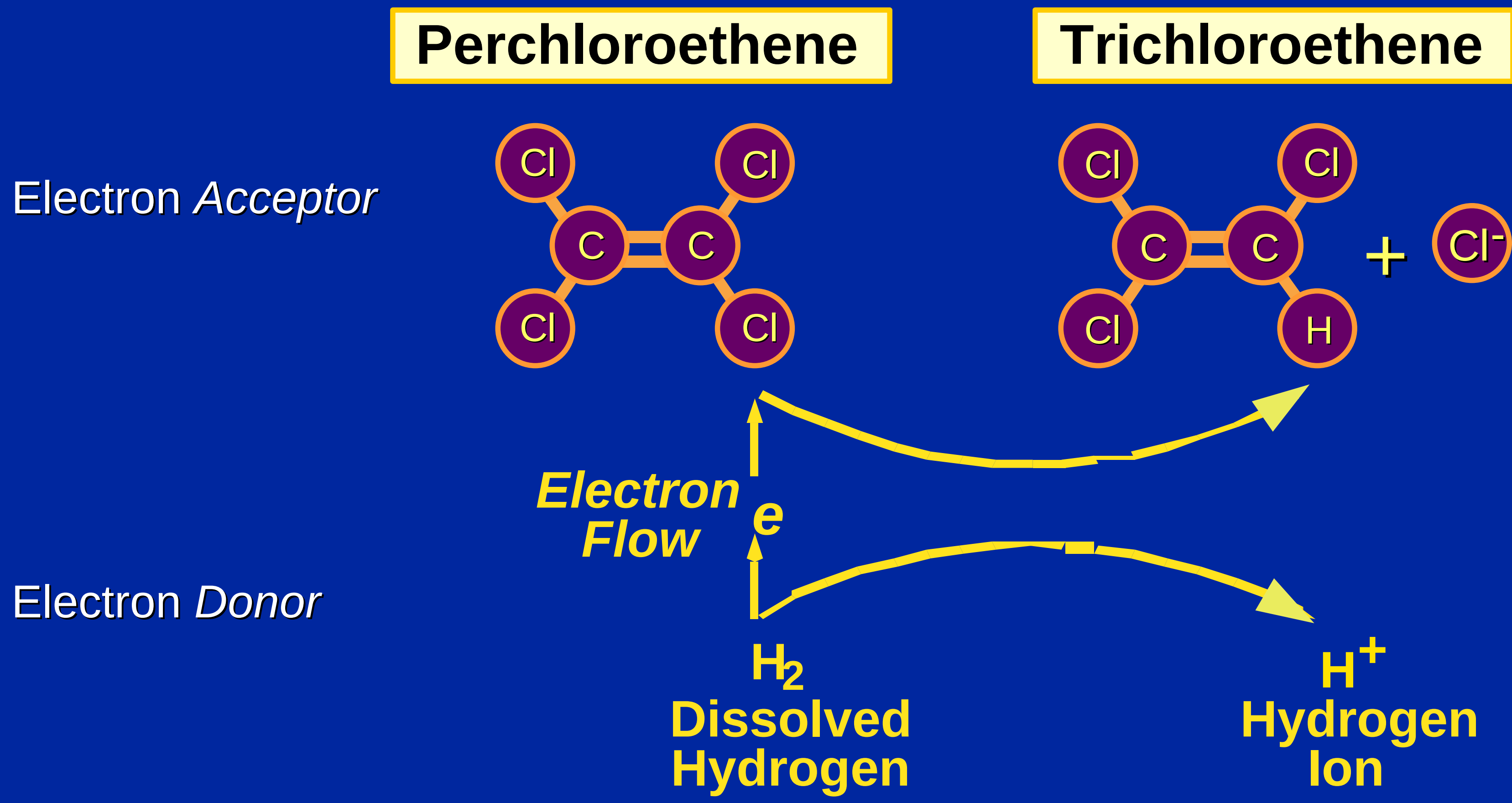
- Use of Organic as Primary Growth Substrate (Direct Biodegradation)

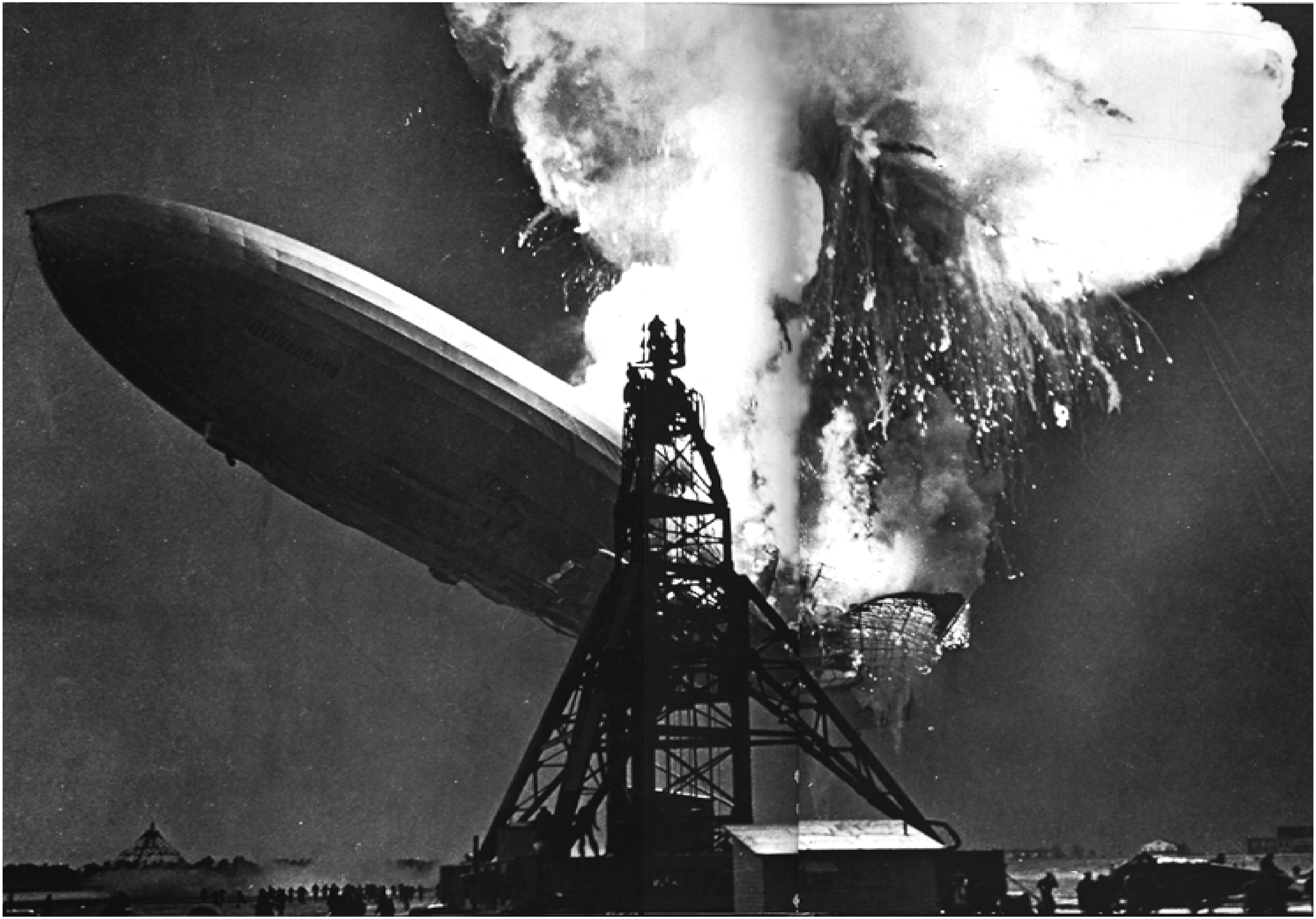
  Degrading organisms gains carbon, energy or both from the degradation of the chlorinated solvent
  - Aerobic Oxidation
  - Anaerobic Oxidation
  - Reductive Dechlorination (“Halorespiration”)
- Cometabolism (Indirect)
  - Chlorinated solvent is fortuitously degraded
  - Occurs under both aerobic and anaerobic conditions
  - Considered less important than direct biodegradation under most conditions

Biological Degradation Processes for Selected Chlorinated Solvents

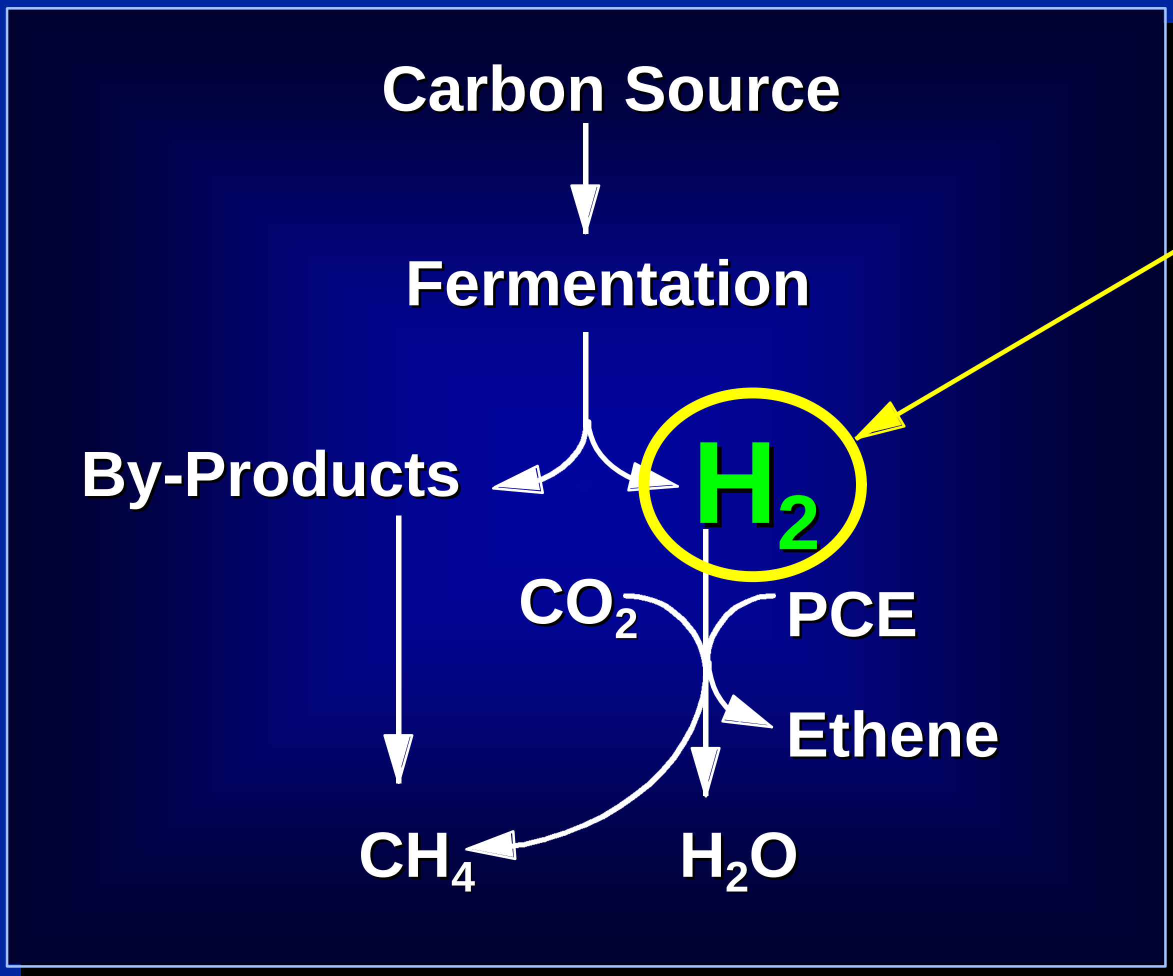
Compound	*Biological Reductive Dechlorination (Halorespiration)*	*Direct Aerobic Oxidation*	*Direct Anaerobic Oxidation*	*Aerobic Cometa-bolism*	*Anaerobic Cometa-bolism*
PCE	✓				✓
TCE	✓			✓	✓
DCE	✓	✓	✓	✓	✓
Vinyl chloride	✓	✓	✓	✓	✓
1,1,1-TCA	✓			✓	✓
1,2-DCA	✓	✓		✓	✓
Chloroethane	✓	✓		✓	✓
Carbon tetrachloride	✓				✓
Chloroform	✓			✓	✓
Methylene chloride		✓	✓	✓	

Reductive Dechlorination Reaction





Production of Electron Donor



Electron Donor; Limits Biodeg.

Requirements for Biological Reductive Dechlorination

- Dechlorinating Bacteria
- Conditions conducive to biological reactions (temperature, pH 6-8,sufficient moisture, absence chemicals toxic to bacteria)
- Electron Acceptor (Chlorinated Solvent)
- Electron Donor (Carbon, Hydrogen)
- Highly Reducing Conditions (Sulfate Reducing or Methanogenic)(e.g., Hydrogen Concentrations > 1 nM)

MNA Terminology

Type I Site: ***Anthropogenic Electron Donor Present (e.g., fuels)***

Type II Site: ***Naturally-occurring electron donor present (e.g., swamps)***

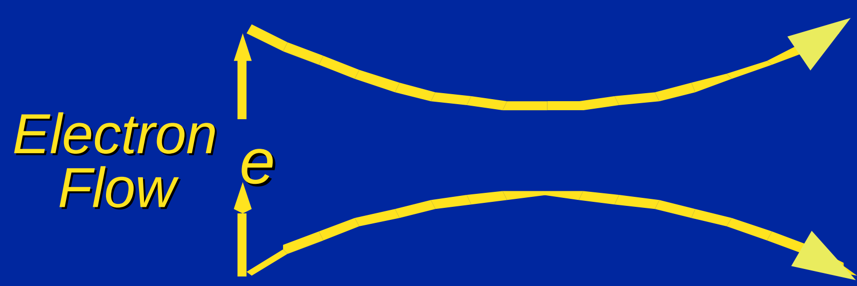
Type III Site: ***No donor present***

Reductive Dechlorination Reaction

Competing Electron *Acceptors*

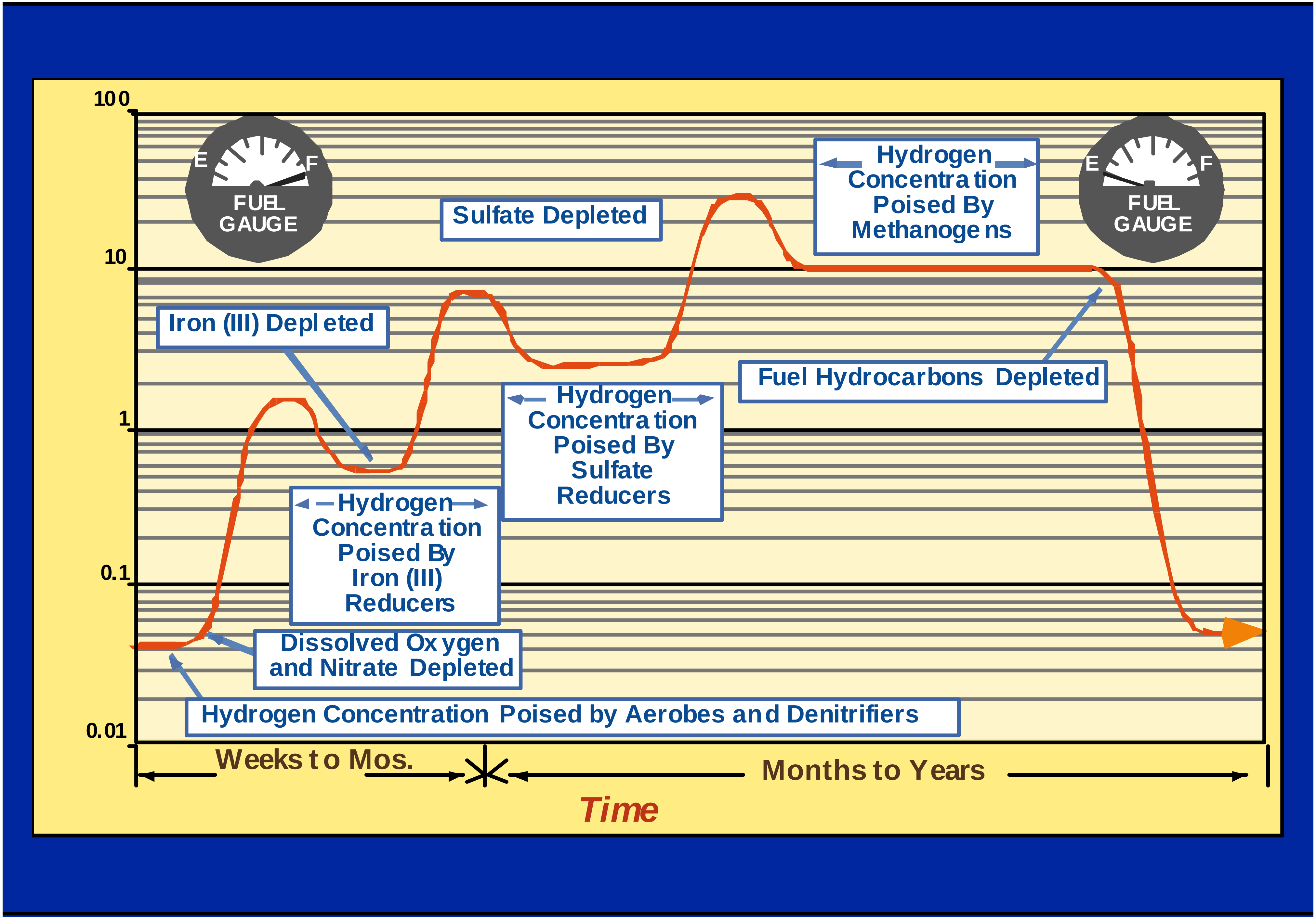
Electron Acceptor		Product
Dissolved Oxygen	→	H_2O
Nitrate	→	N_2
Ferric Iron	→	Ferrous Iron
Chlorinated Solvent	→	Daughter Product
Sulfate	→	H_2S
Methanogens	→	Methane

Electron Donor



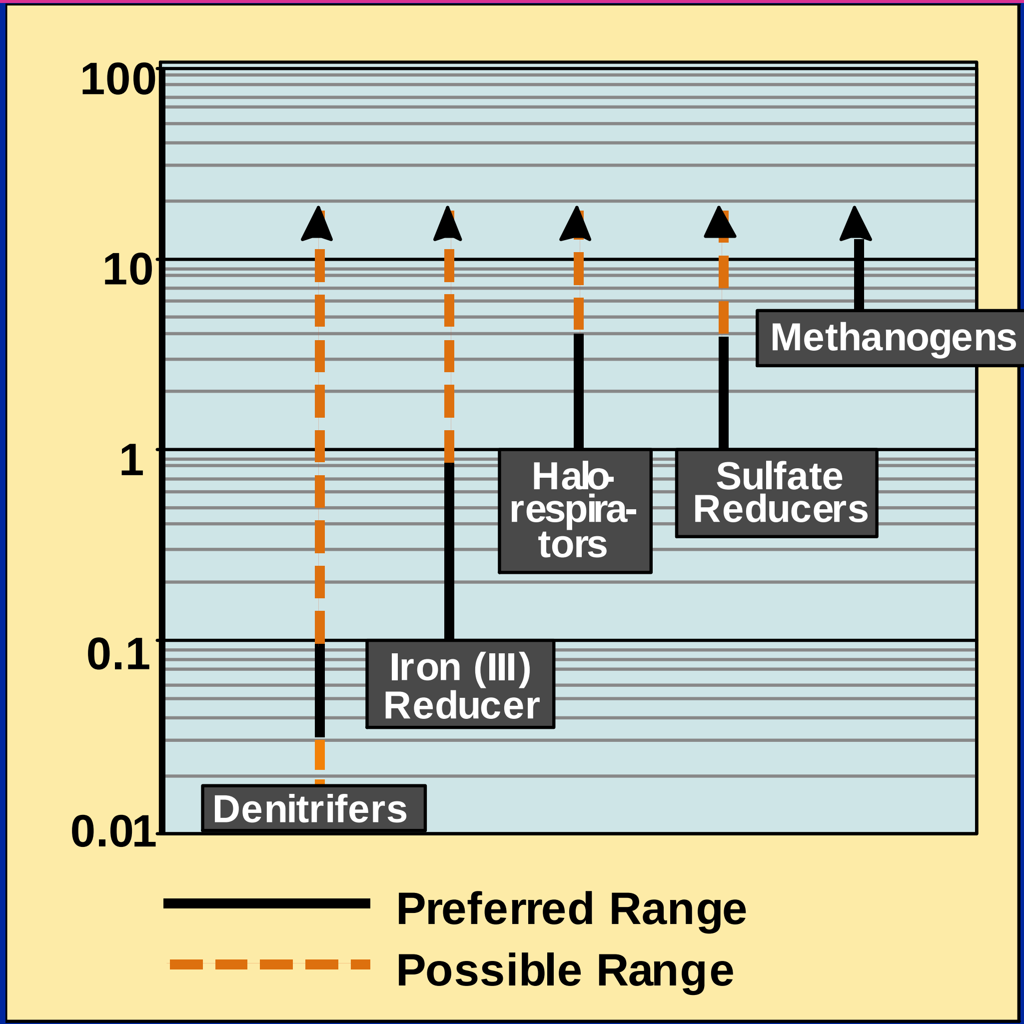
H_2
Dissolved Hydrogen

H^+
Hydrogen Ion



100
10
1
0.1
0.01
FUEL GAUGE
E
F
Sulfate Depleted
Hydrogen Concentration Poised By Methanogens
Iron (III) Depleted
Hydrogen Concentration Poised By Sulfate Reducers
Fuel Hydrocarbons Depleted
Hydrogen Concentration Poised By Iron (III) Reducers
Dissolved Oxygen and Nitrate Depleted
Hydrogen Concentration Poised by Aerobes and Denitrifiers
Weeks to Mos.
Months to Years
Time

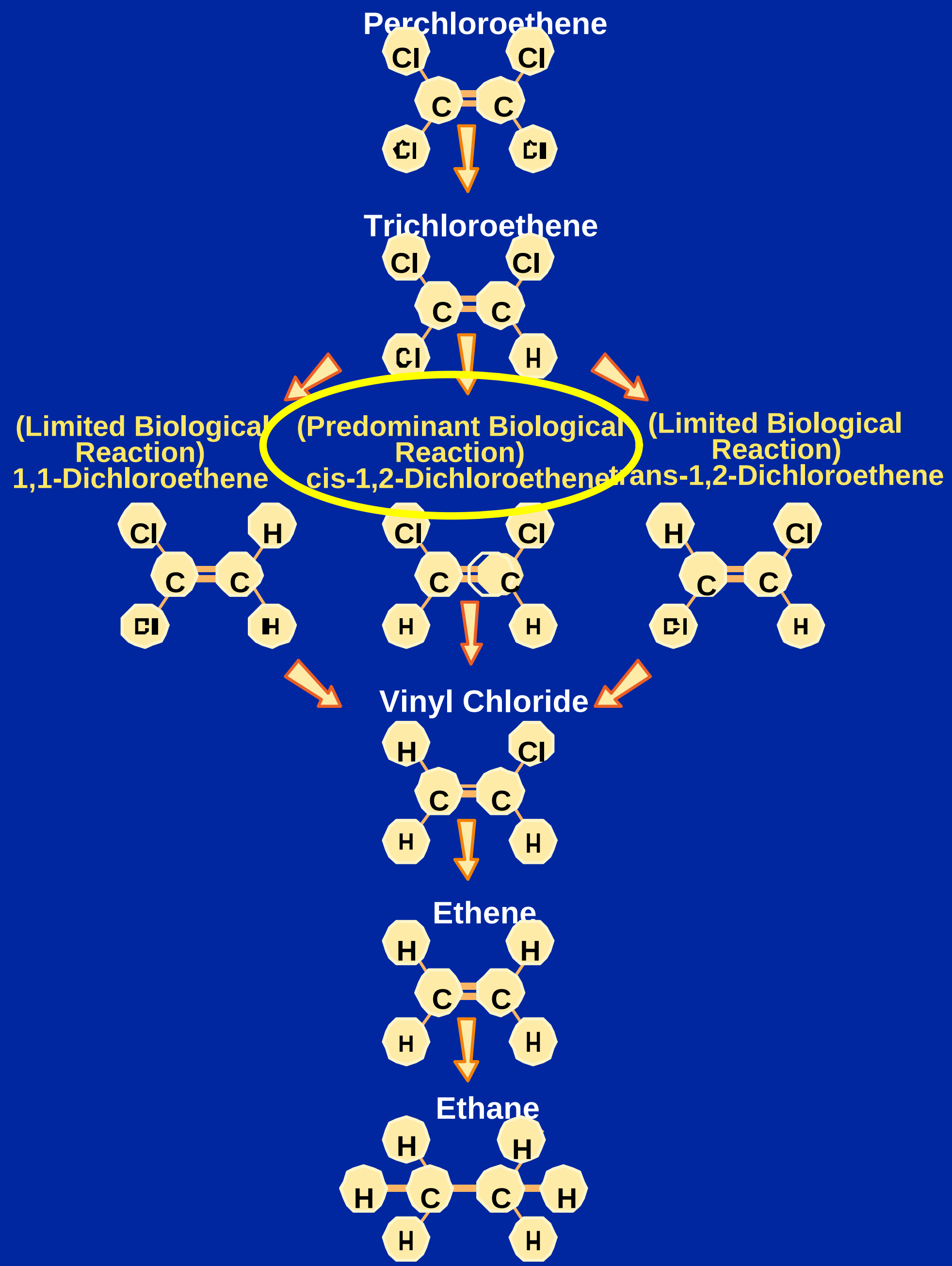
Range of Hydrogen Concentrations Where Anaerobic Reactions Are Observed



Footprints

Geochemical Footprints: BTEX	• *Dissolved oxygen depletion* • *Nitrate depletion* • *Ferrous iron production* • *Sulfate depletion* • *Methane production*
Geochemical Footprints : Anaerobic Biodegradation of Chlor. Solvents	• *Daughter product production* • *Ethene/Ethane production* • *Chloride product (hard to see)* • *Low dissolved oxygen (shows condition ok)* • *Methane production (shows condition ok)*
Geochemical Footprints : Aerobic Biodegradation of Chlor. Solvents	• *Daughter product production* • *CO_2 production (hard to see)* • *Chloride production (hard to see)* • *Dissolved oxygen depletion*

Reductive Dechlorination of Chlorinated Ethenes

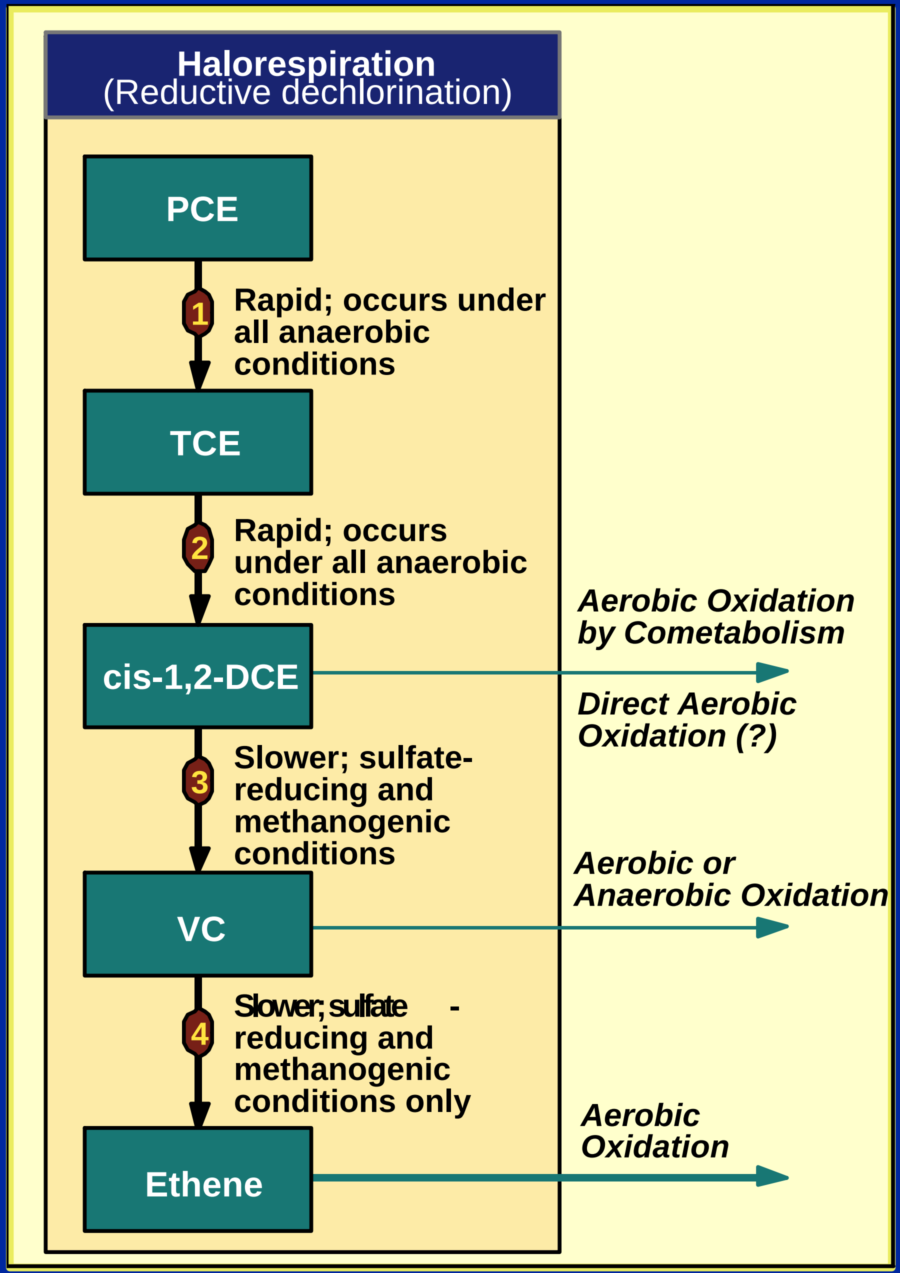


Key footprint of PCE or TCE biodegradation: presence of cis 1,2-DCE

Biodegradation Pathway for Chlorinated Ethenes

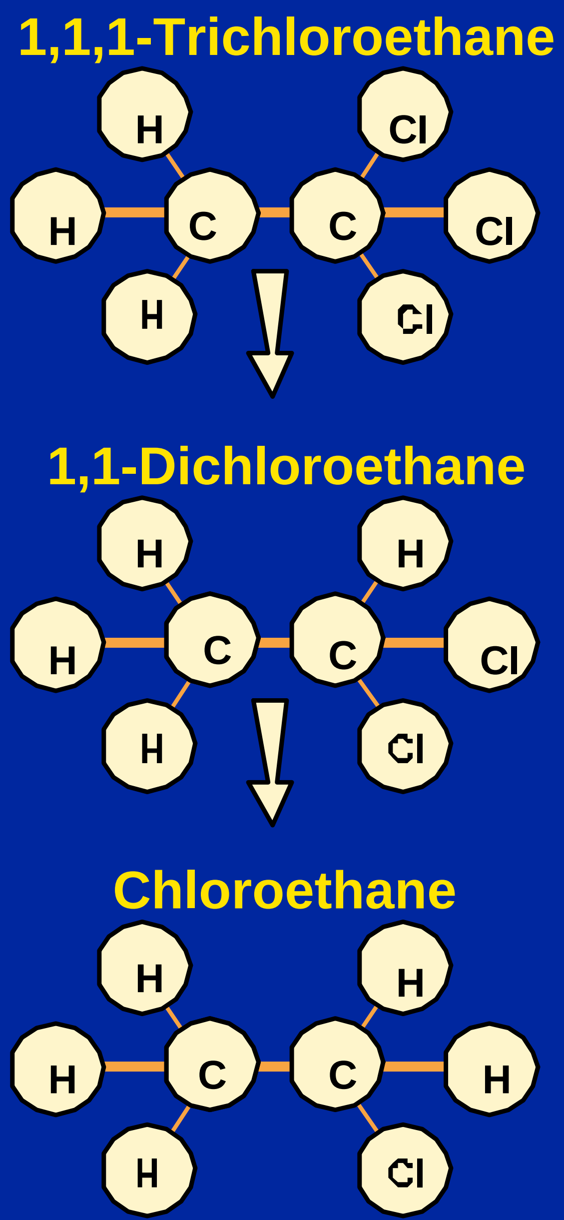
Key footprints of PCE or TCE biodegradation:

presence of cis-DCE, VC, ethene, ethane

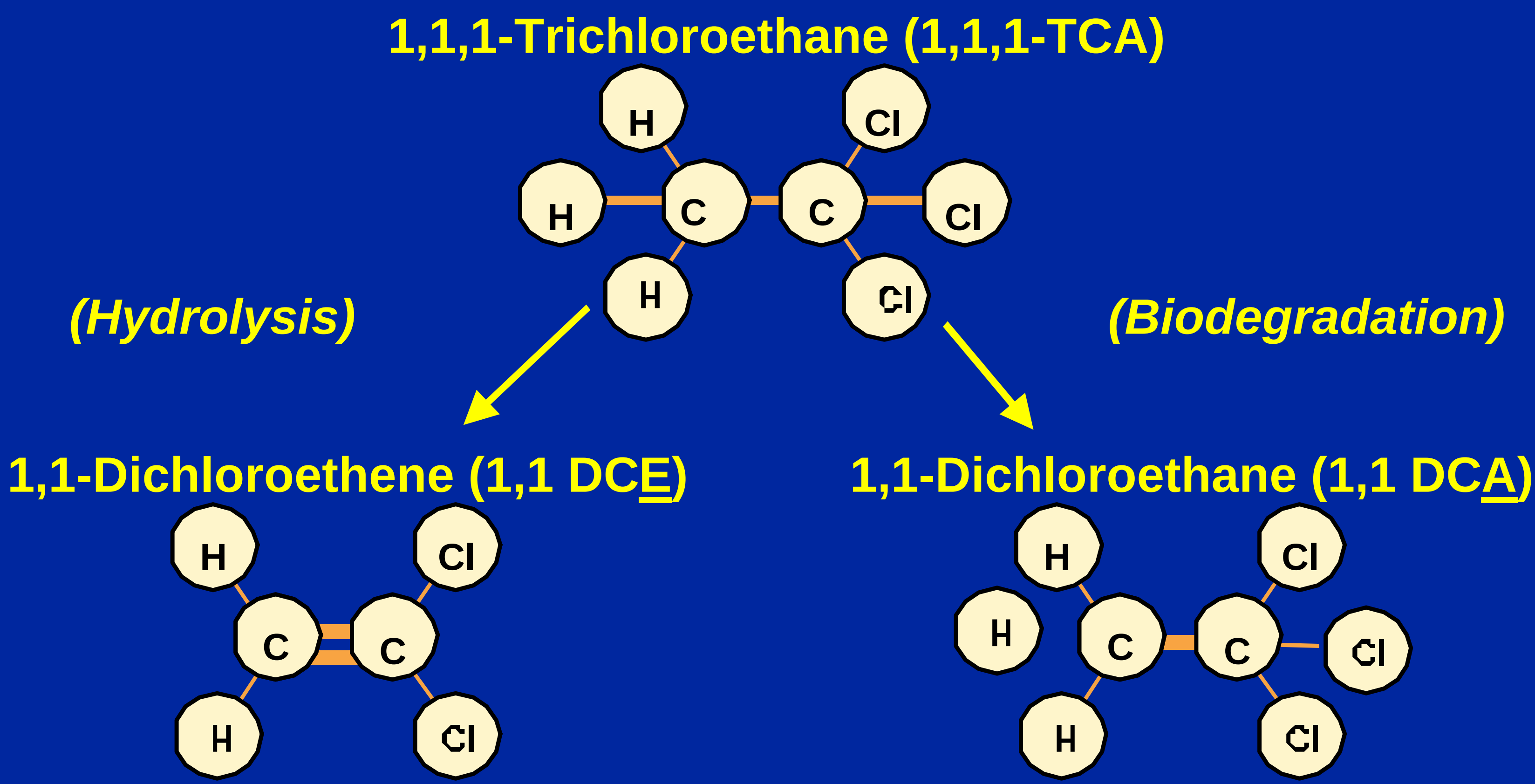


(Adapted from RTDF, 1997.)

Reductive Dechlorination of Chlorinated Ethanes



Degradation Pathways of 1,1,1 TCA



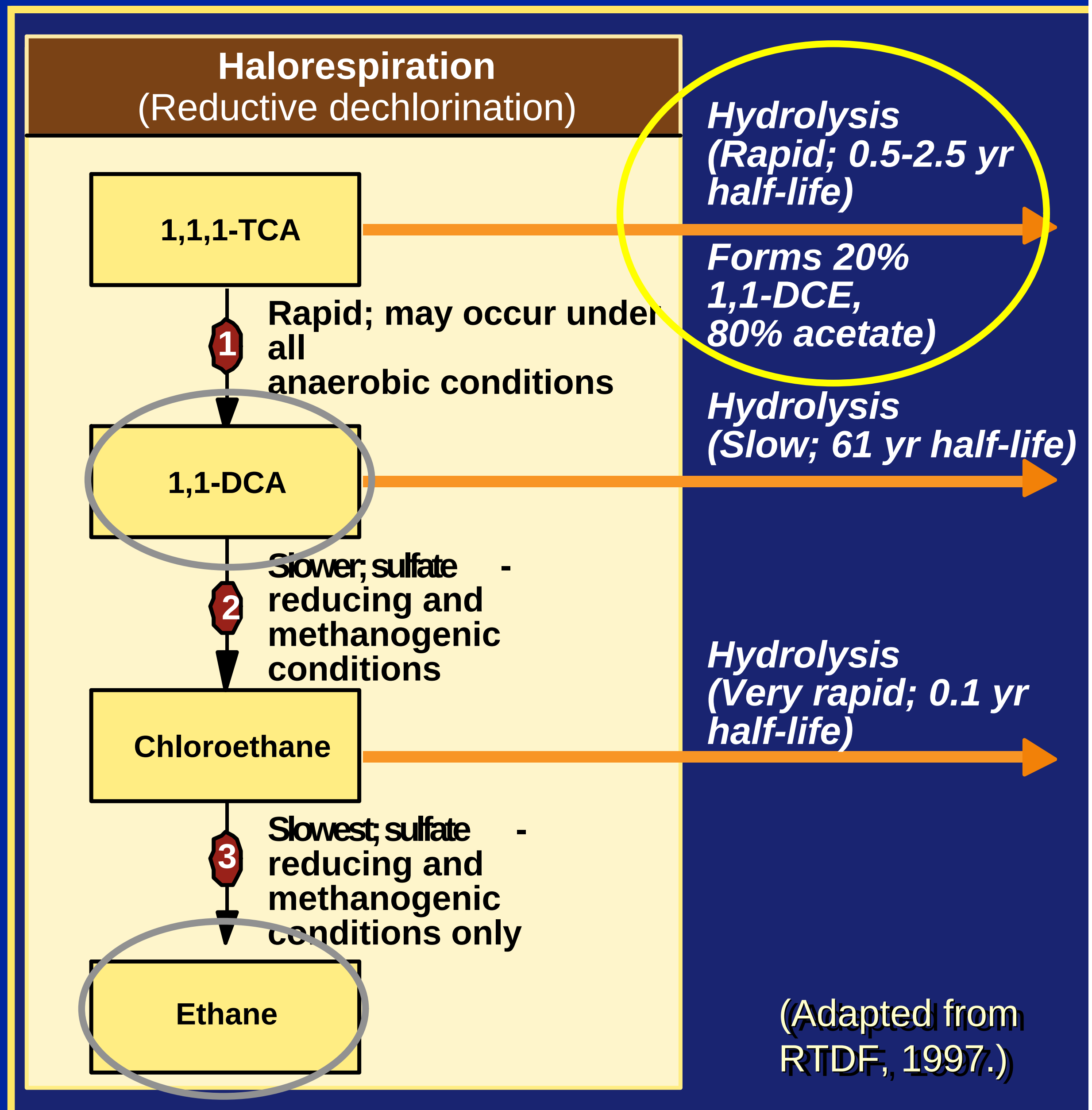
Degradation Pathway for Chlorinated Ethanes

Key footprints of 1,1,1-TCA chemical degradation:

presence of 1,1-DCE

Key footprints of 1,1,1-TCA biodegradation:

presence of 1,1-DCA, ethane



Conditions Which Inhibit Solvent Degradation

PCE: Aerobic conditions (not enough natural donor)
TCE: Aerobic conditions (not enough natural donor)
cis-DCE: some sites don't seem to degrade cis-DCE because
- right bugs aren't there (need bioaugmentation)?
- system not anaerobic enough?

VC: Not aerobic or anaerobic enough

TCA: None (except temperature?) (will always get hydrolysis)
1,2-DCA: ?
1,1-DCE: ?
Chloroethane: None (very fast hydrolysis)

BIOCHLOR Database

A Statistical Study of Chlorinated Solvent Sites

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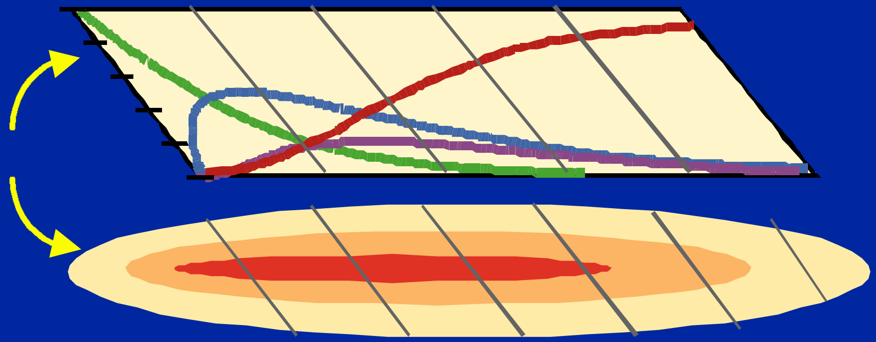


Objectives of Study

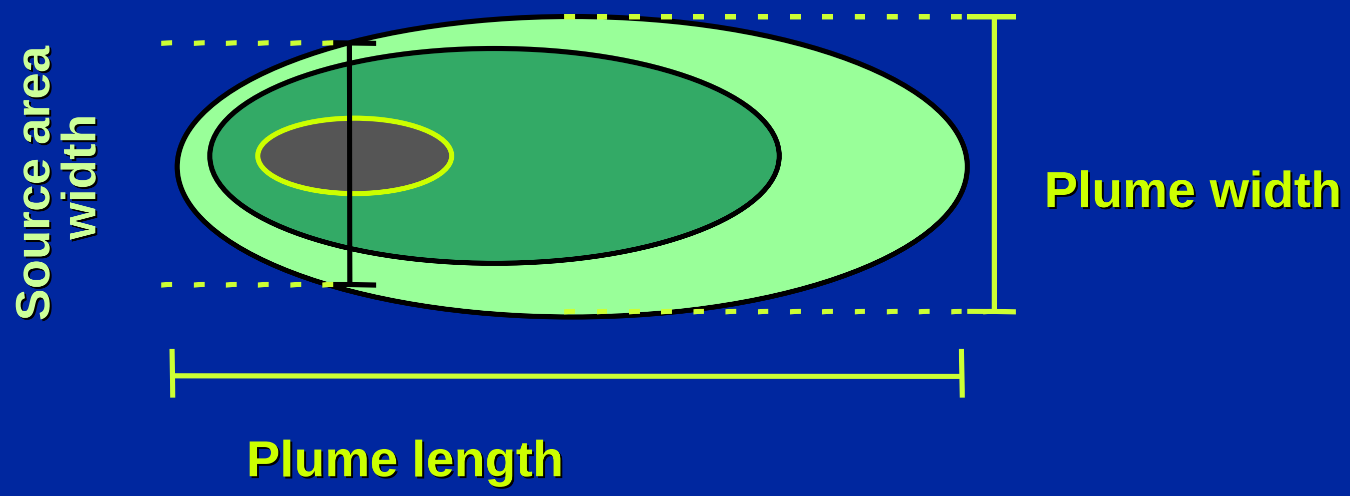
- Identify key characteristics of parent and daughter plumes
- Determine important relationships between plume, hydrogeology, source
- Estimate rate constants

To be used by site managers to:

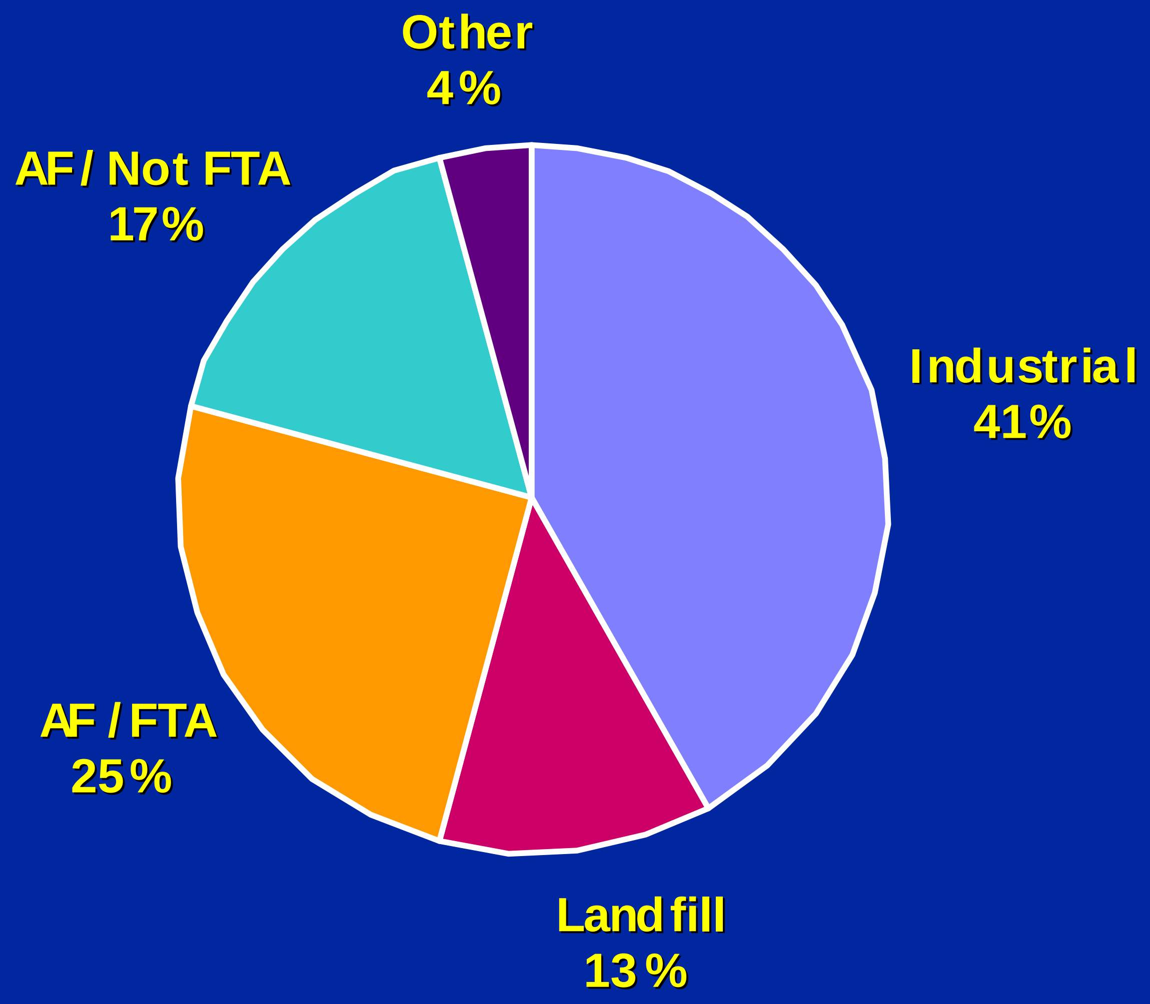
- E*stimate* plume lengths and migration
- Estimate potential effectiveness of natural attenuation

Methodology

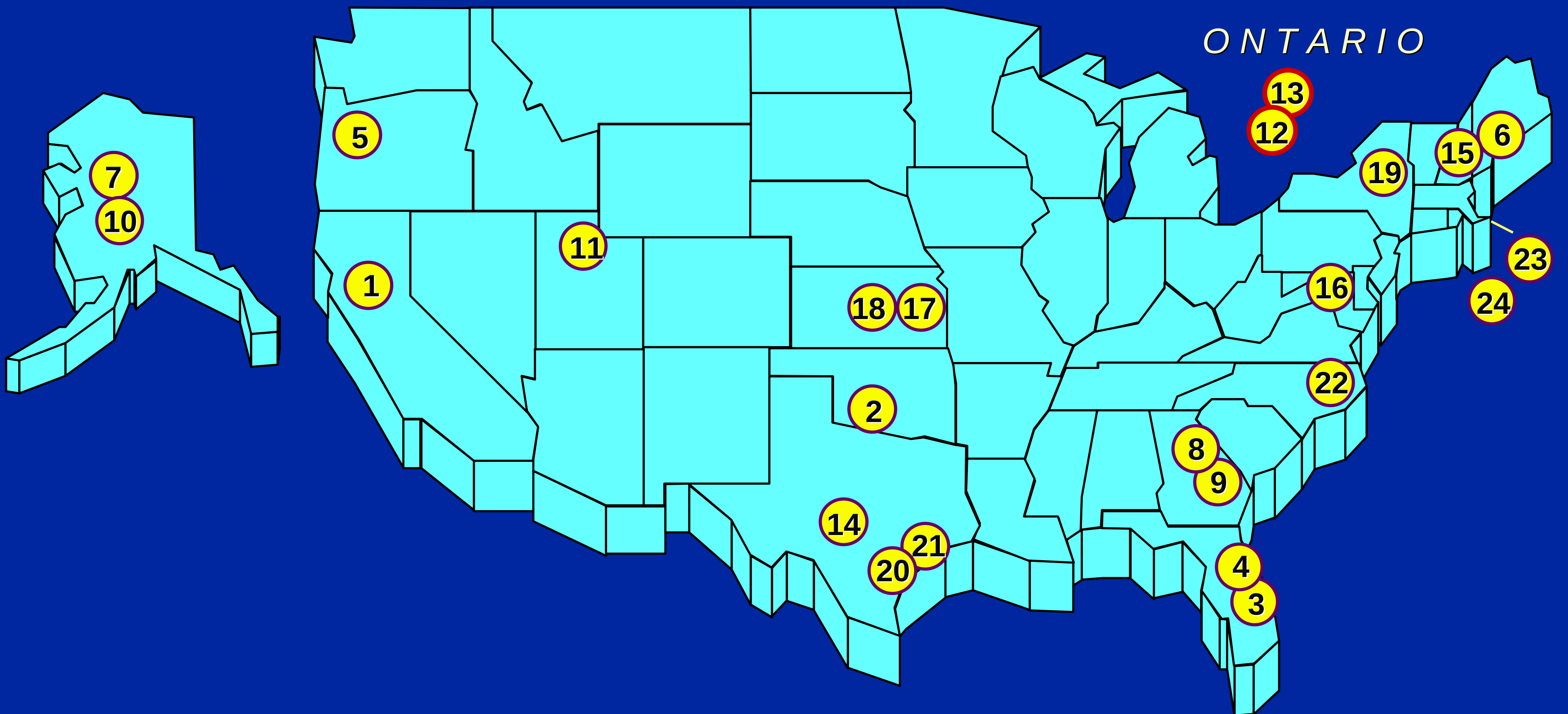
- Based on Questionnaire for 24 sites.
- Mean hydrogeologic property values and chlorinated solvent concentration data extracted from reports for most contaminated unit.
- Plume lengths determined from isopleth data in site reports.



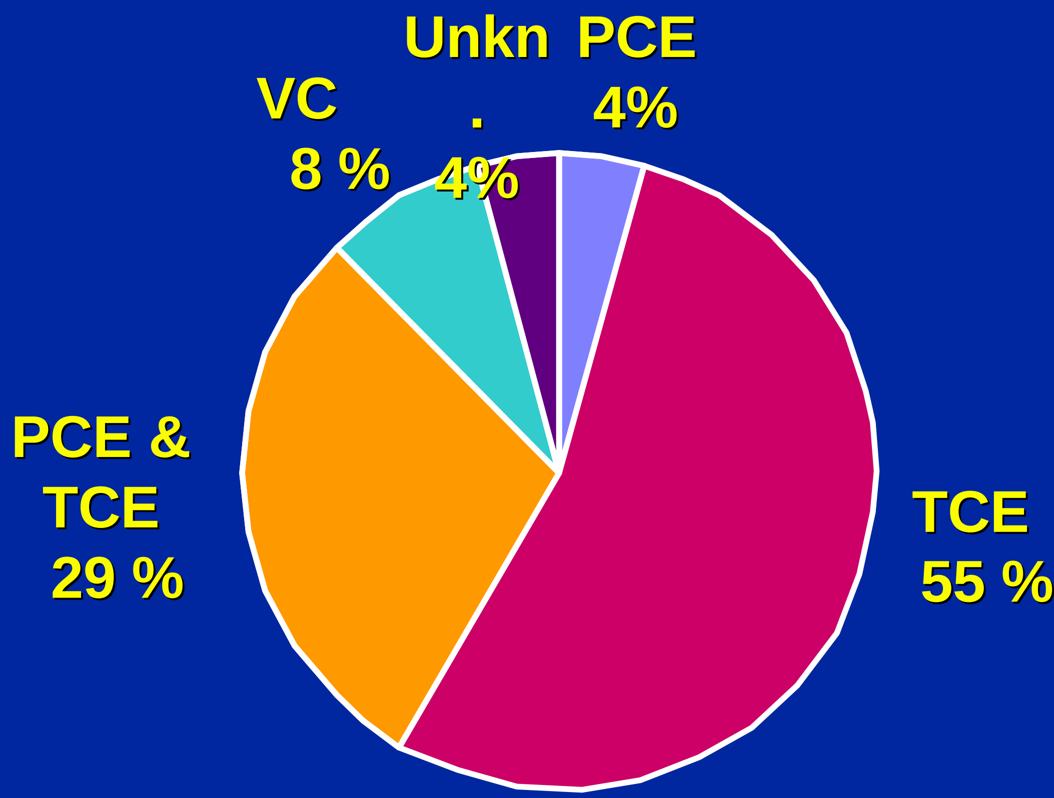
Site Type



Location of Sites In Database



Parent Compounds

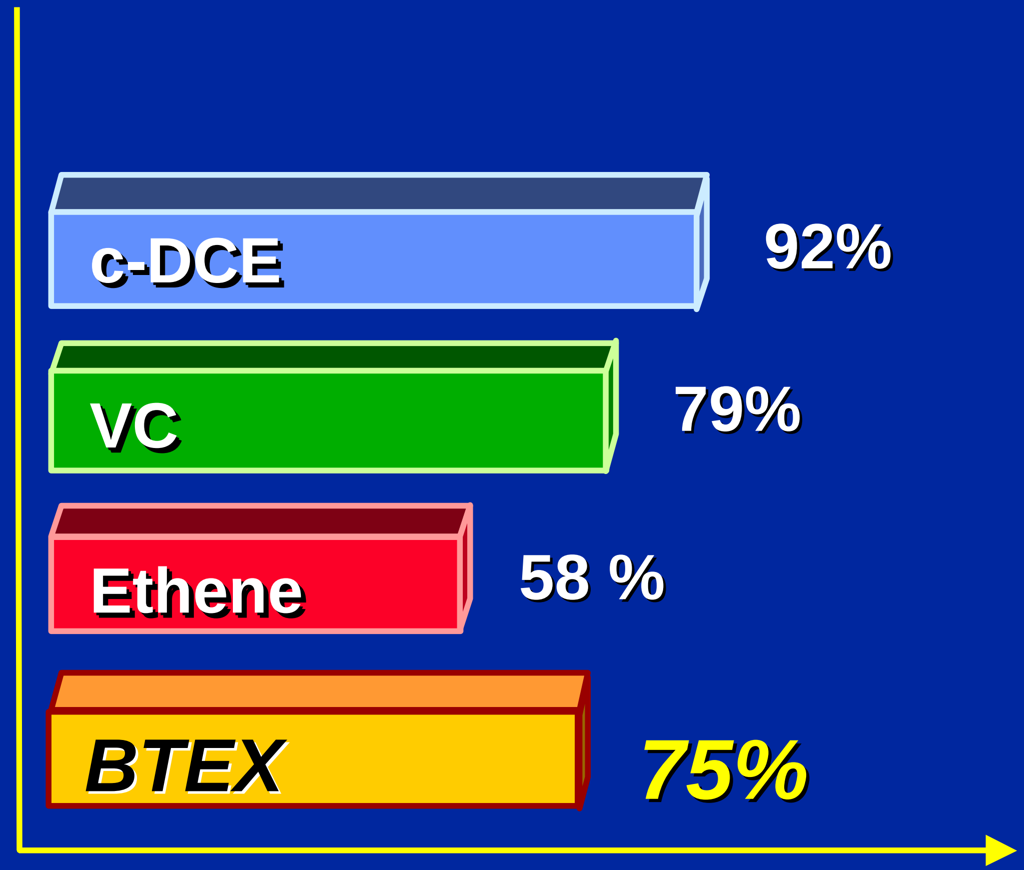


BIOCHLOR Database

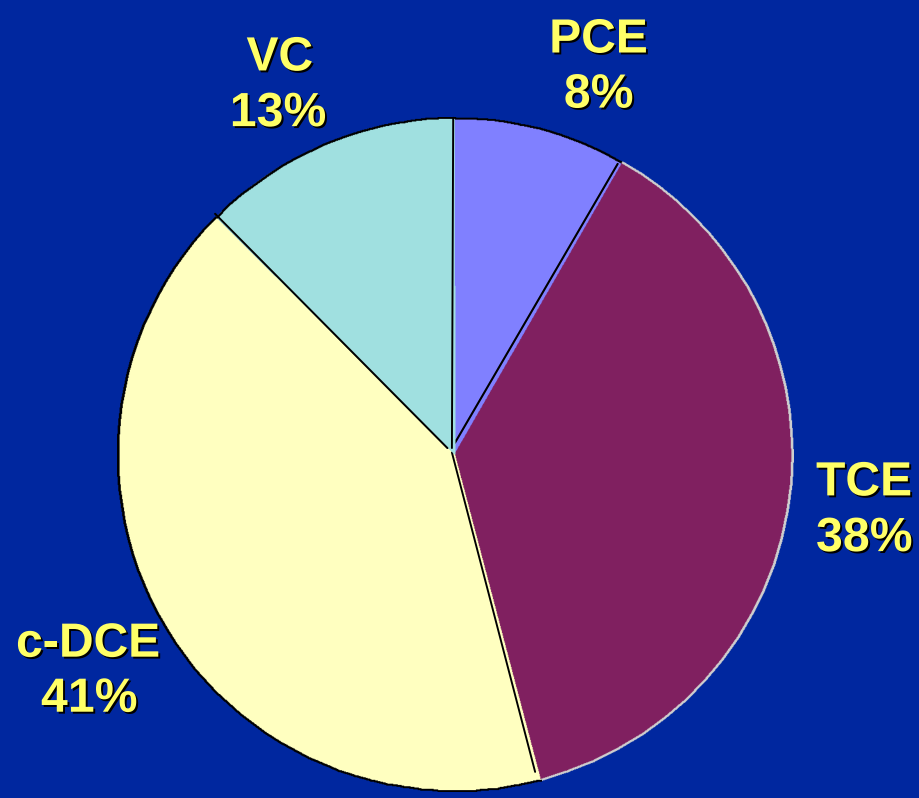
- Showed considerable biotransformation
  - decrease in parent compounds
  - c-DCE presence - long plumes, high concentrations
  - chloride ion production
  - presence of ethene

⇨ reductive dechlorination

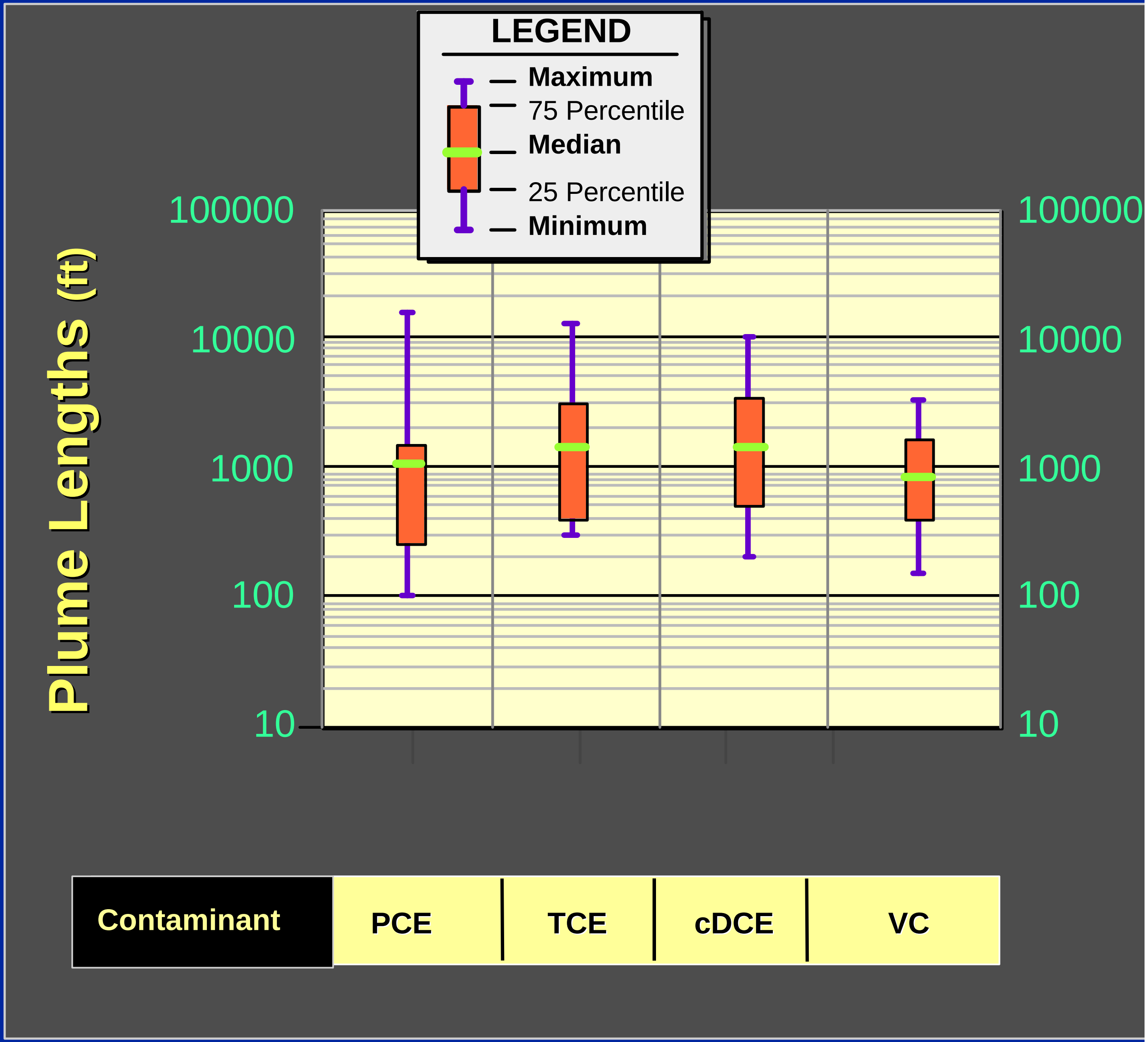
Incidence of Daughter Products at BIOCHLOR Sites



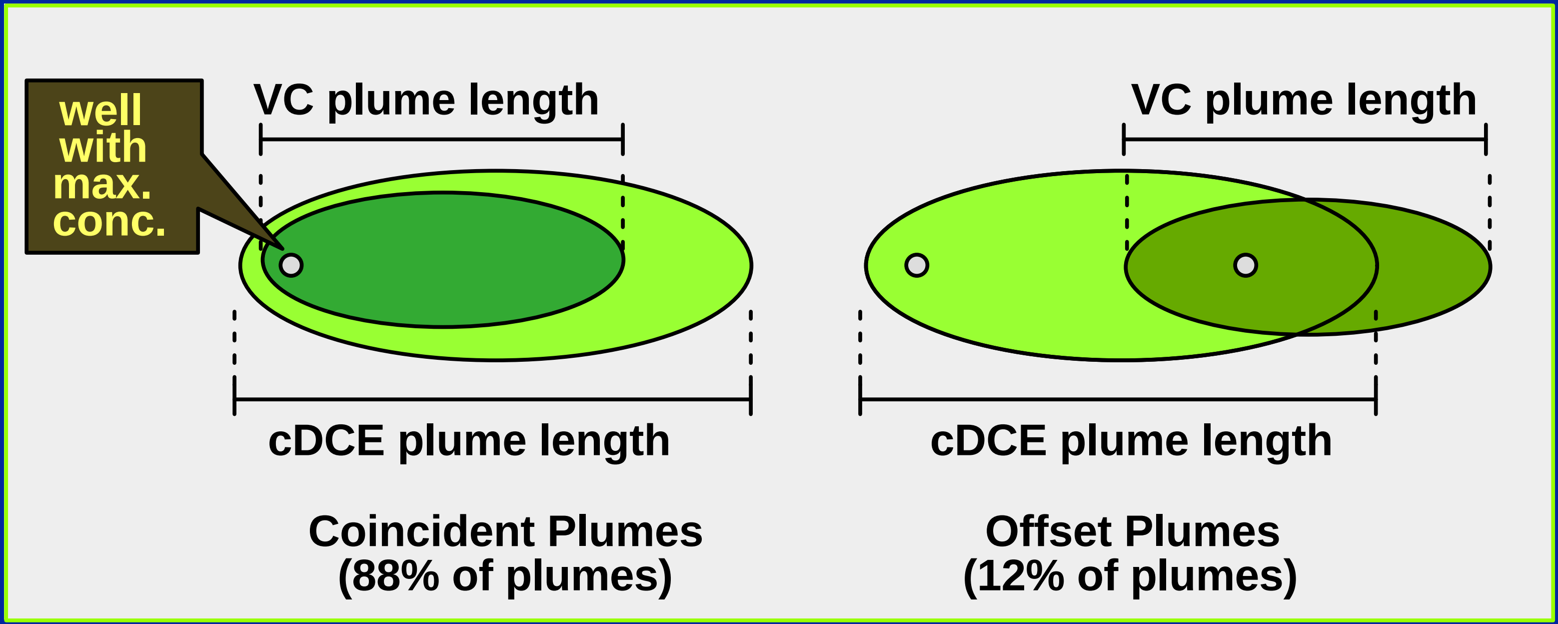
Longest Plumes: *Chlorinated Ethenes*



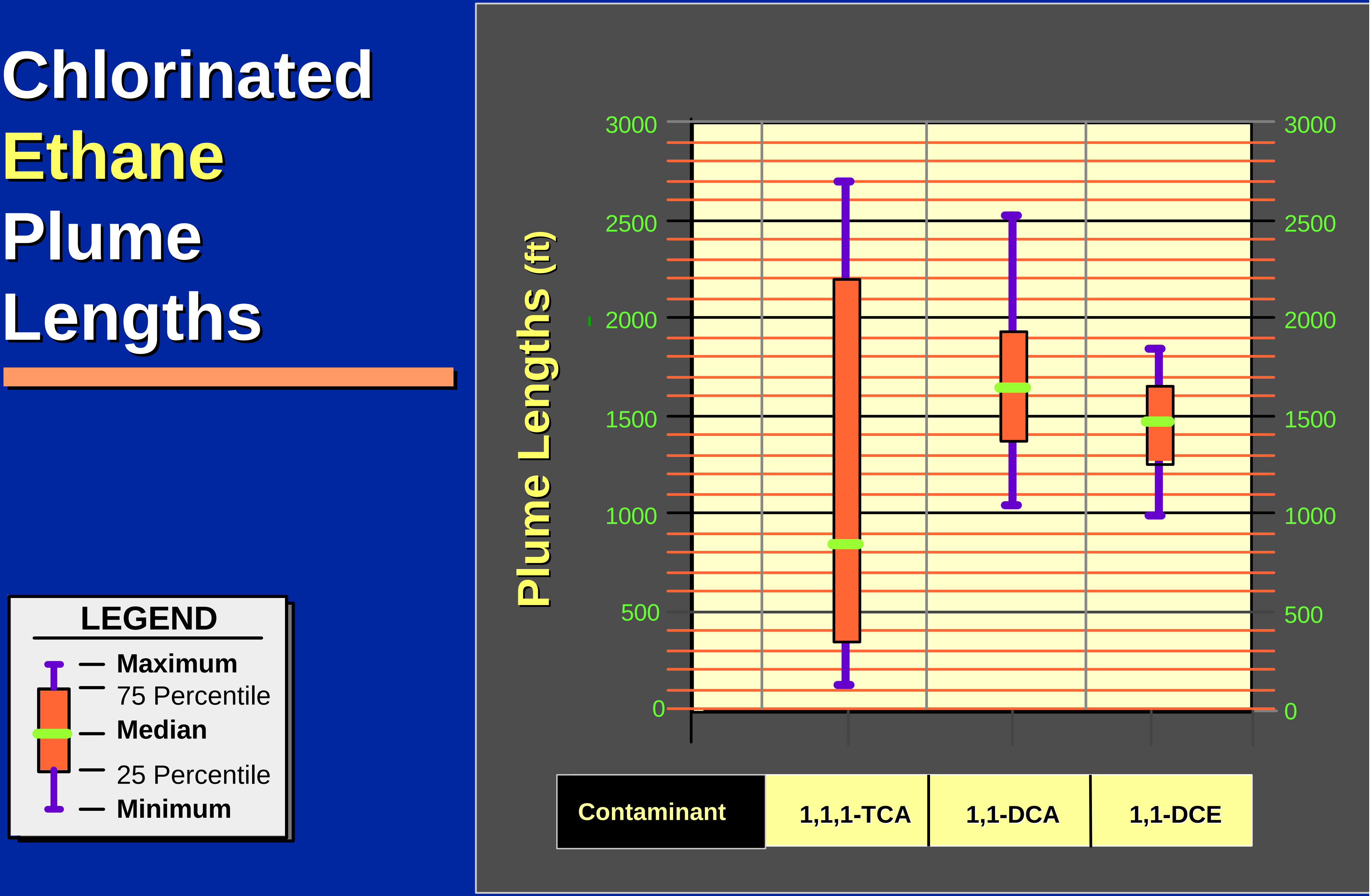
Chlorinated Ethene Plume Lengths



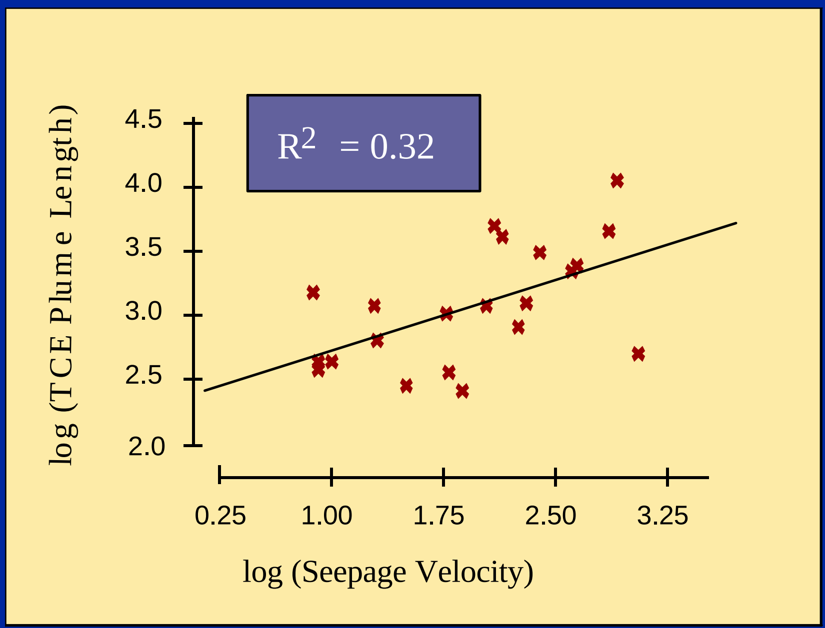
Plume Coincidence

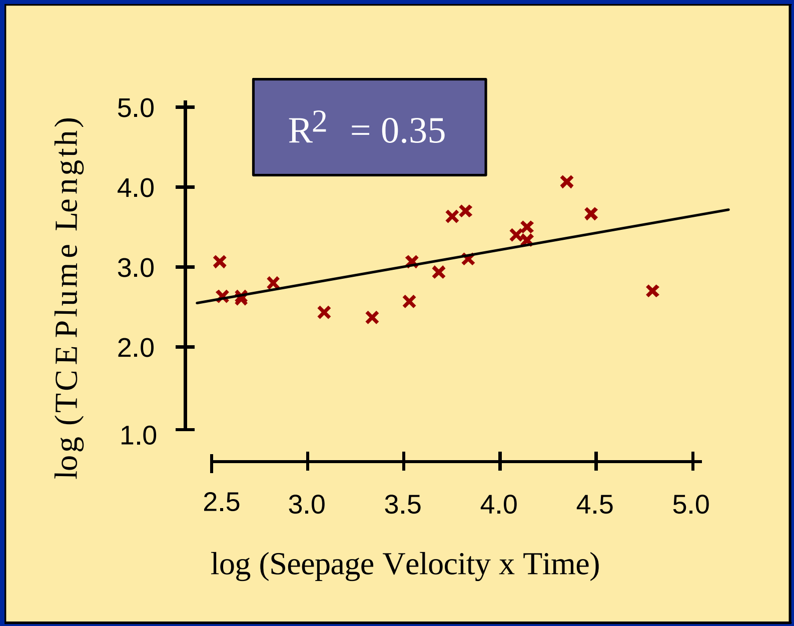


Chlorinated Ethane Plume Lengths



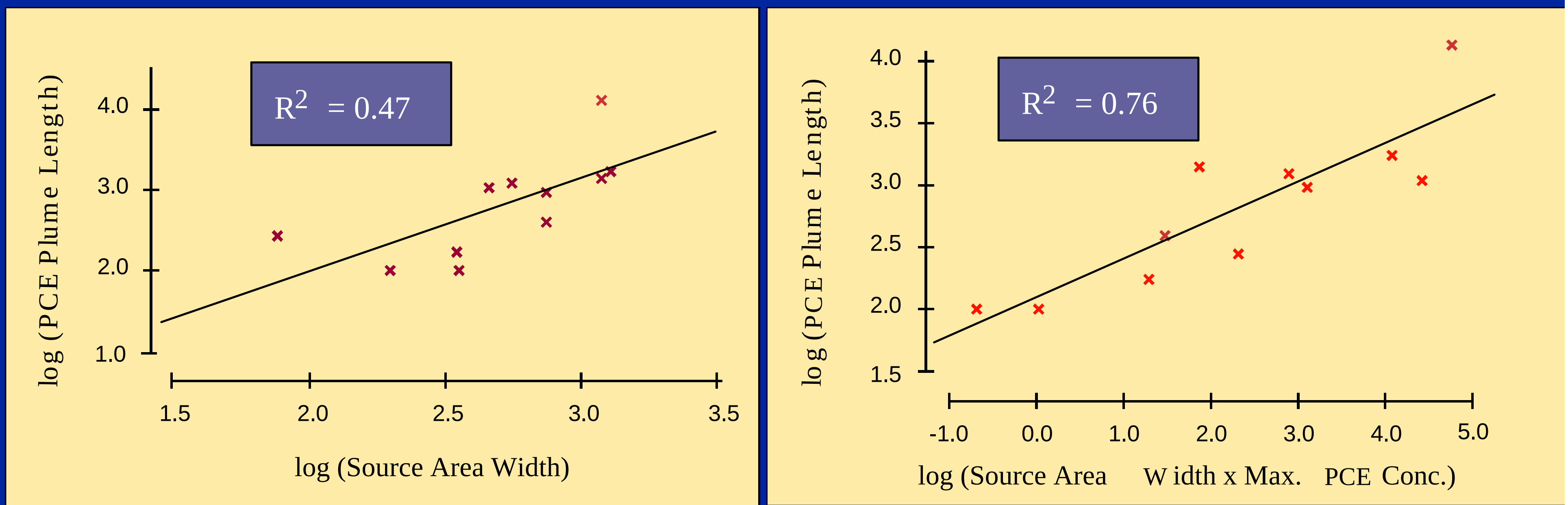
Effect of Advection





Moderate effect of advection on plume length

Effect of Source Size and Strength



- **Stronger effect of advection on plume length**

Important Factors Impacting Chlorinated Solvent Plumes

- *Advection*
- *Source Size and Strength*

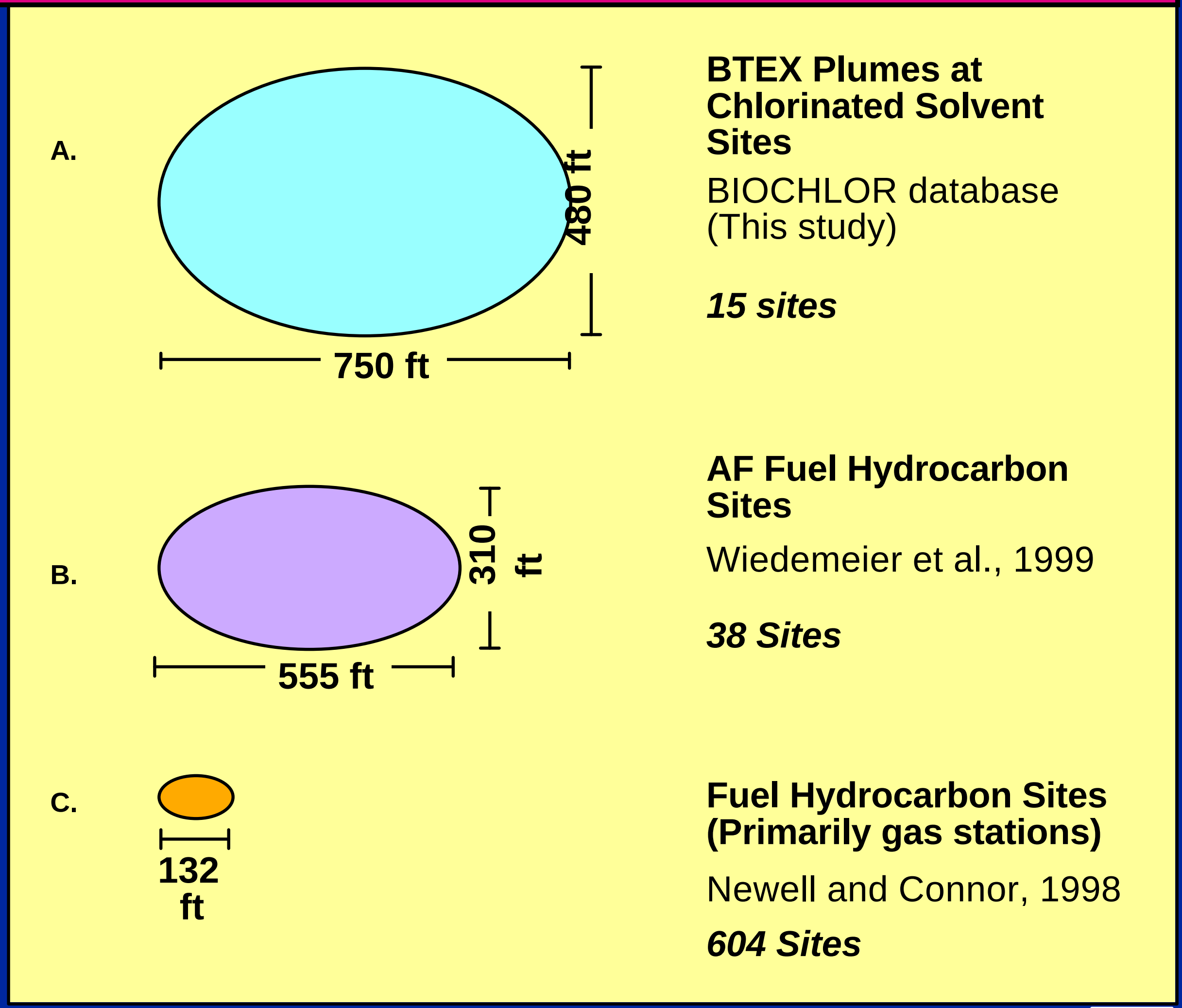
KEY POINTS:

1) **Plumes will be shorter at sites with slow regional groundwater flow and small source areas.**

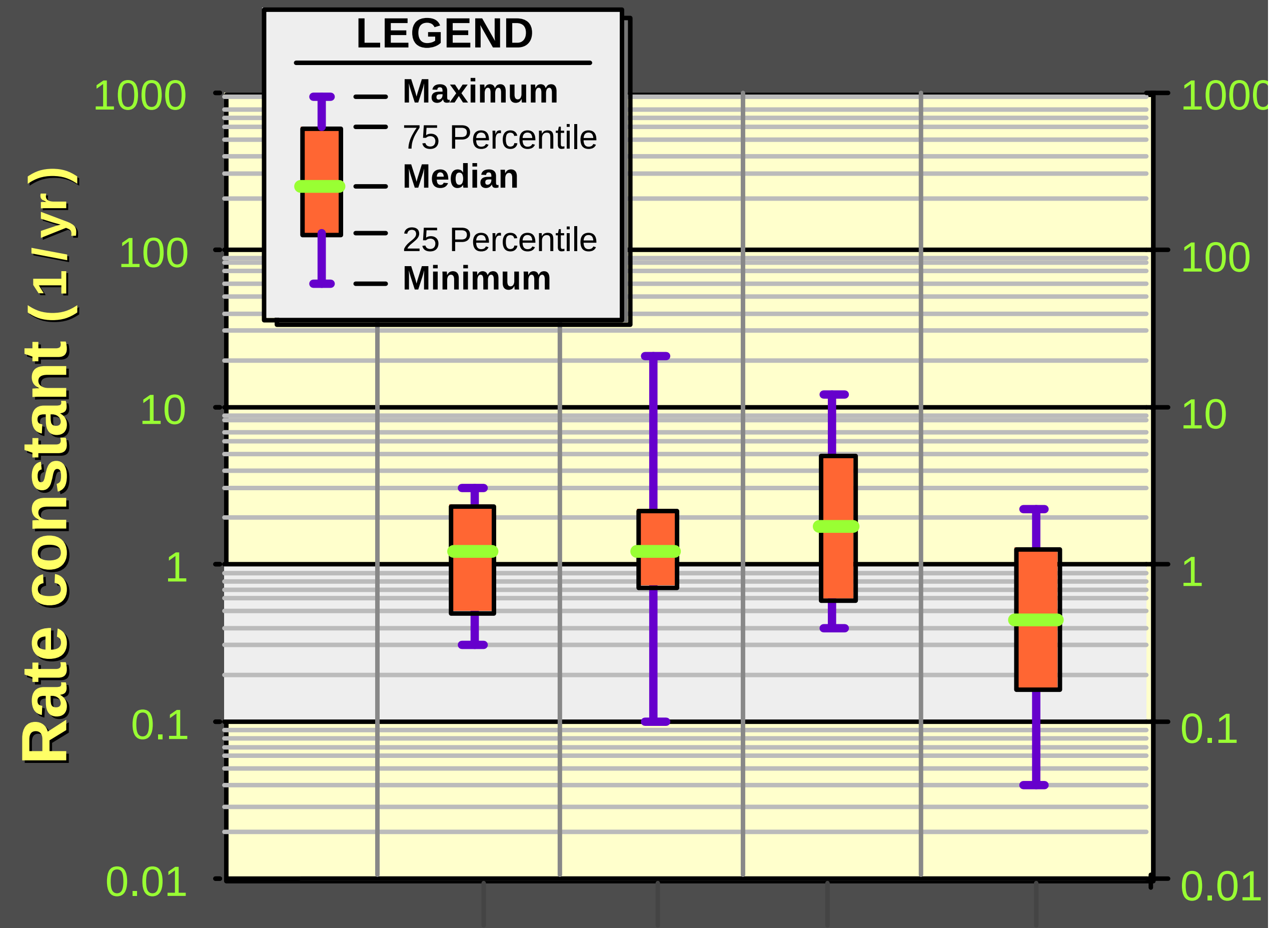
2) **Information from source area alone can be helpful in estimating plume lengths.**

BTEX Plume Characteristics at Chlorinated Solvent Release Sites

- ***BTEX Plumes much longer at chlorinated solvent sites.***
- ***Related to source width and DNAPL.***



BIOCHLOR Rate Constants



Contaminant	TCE	cDCE	VC	BTEX
Source	This study	This study	This study	Wiedemeier et al., 1995
Number of Sites	10	9	7	23

Key Conclusions

- Median plume lengths of chlorinated solvents range from 860 to 1470 ft.
- TCE or c-DCE most likely to be the longest plume, VC the shortest.
- Widespread evidence of reductive dechlorination was found (i.e., presence of c-DCE, VC, ethene, and increased concentrations of chloride).

Key Conclusions *(Cont'd)*

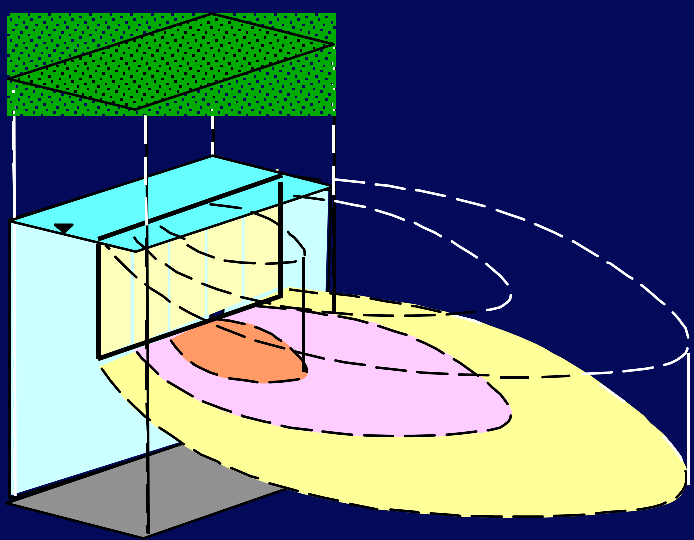
- Source area size and strength and groundwater velocity best predictors of solvent plume length
- Solvent plumes will be shorter at sites with low groundwater velocities and weak, small source areas

BIOCHLOR Road Map

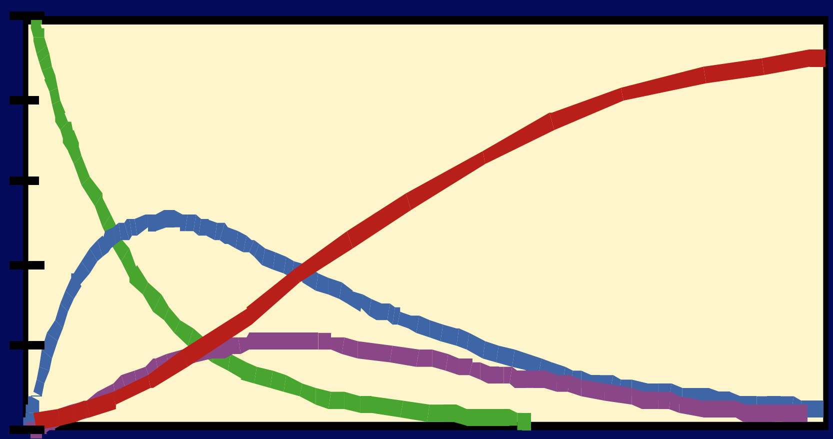
- Chlorinated Solvent Biodegradation
- BIOCHLOR "Plume-a-thon" Study
- ➡ **How BIOCHLOR Works**

BIOCHLOR Model

Domenico Solution for Groundwater Transport



Reductive Dechlorination/ Sequential First Order Rxns



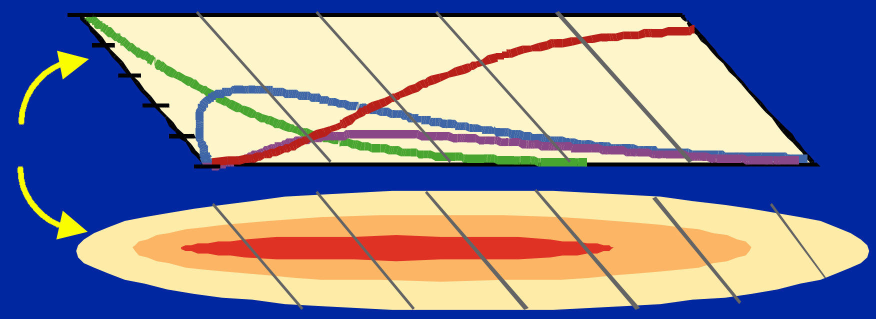
Why Use BIOCHLOR?

- Method for Estimating Plume Lengths
- System to Organize Site Data
- Tool to Help Understand Site Processes
- Screening Tool for Applicability of NA
- Supporting Line of Evidence for NA

BIOSCREEN vs. BIOCHLOR: *Similarities*

- Domenico Analytical Model
- Microsoft Excel Platform
- User-Friendly Interface
- Based on Site Database
- Free Over the Internet

BIOCHLOR: Key Processes



- Advection (1-D)
- Dispersion (3-D)
- Sorption
- Biodegradation:
  - Reductive dechlorination
  - Sequential reactions (parents to daughters)
  - Limited hydrolysis
- Different biodegradation zones

First-Order Decay Model

The decay rate is usually assumed to be first order:

$$\text{rate} = -\, l\; C_t$$

$$\frac{dC_t}{dt} = -\, l\; C_t$$

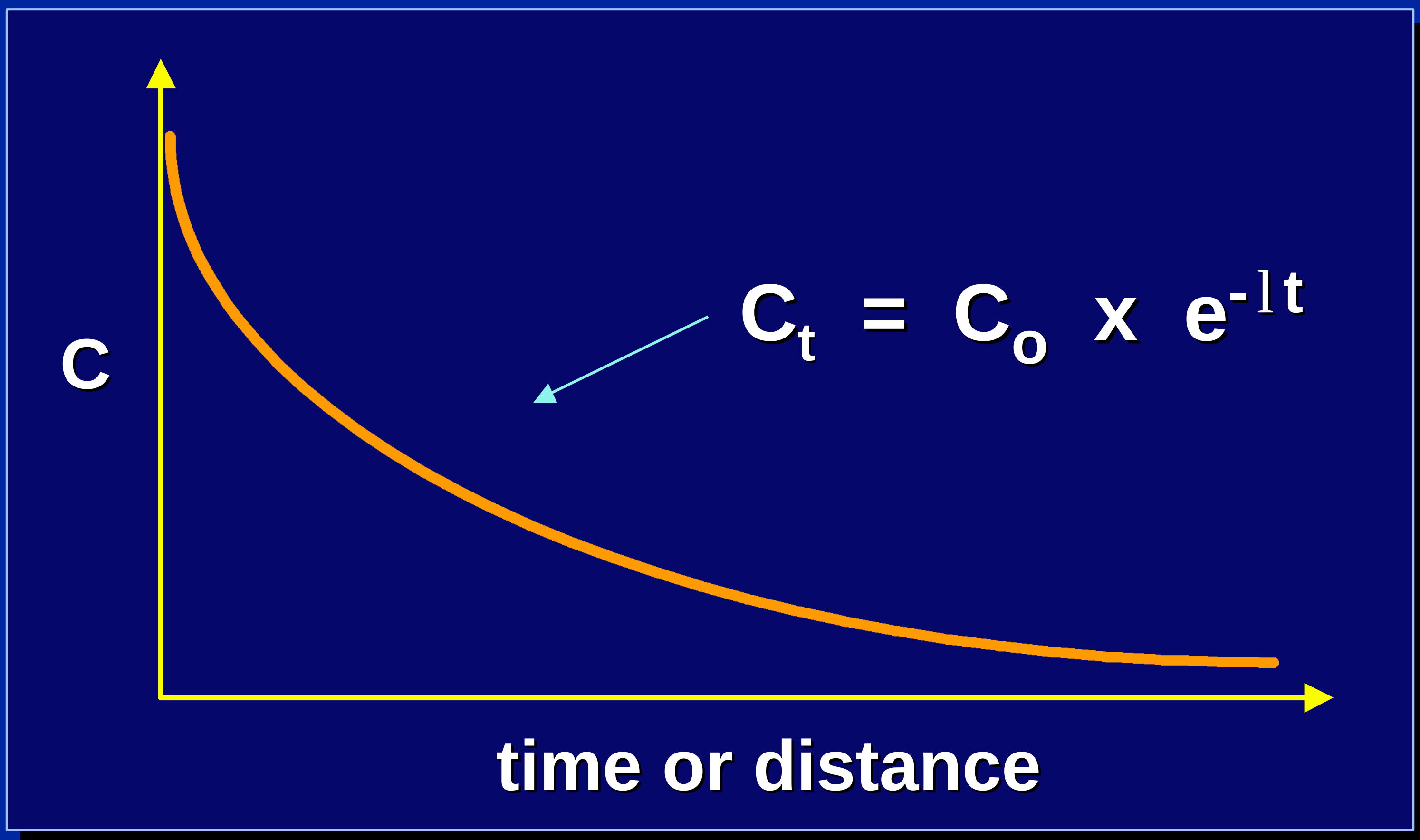
$$C = C_o \exp(-\, l\, t)$$

C_t = concentration at time t (mg/l)

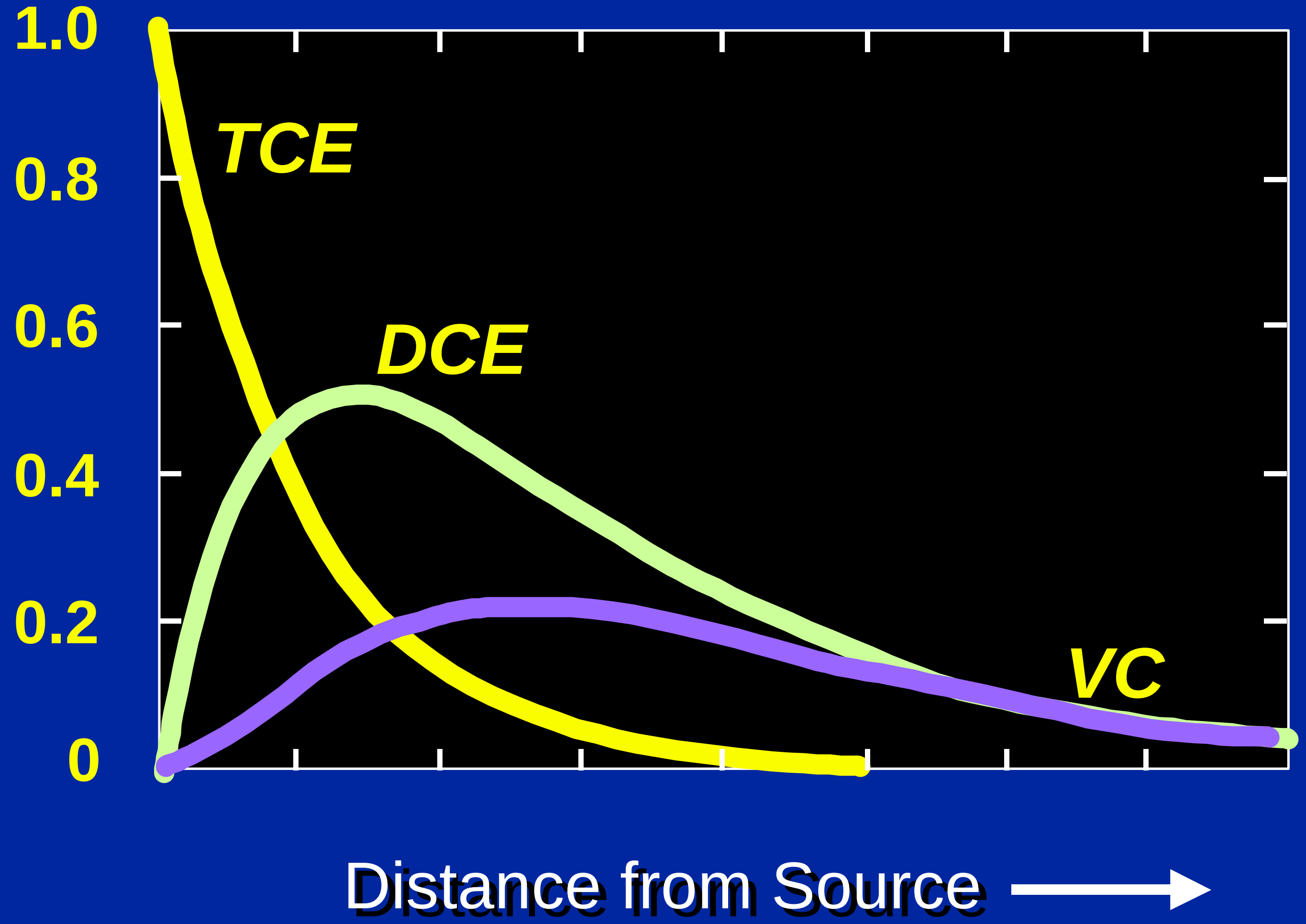
C_o = concentration at time 0 (mg/l)

l = first order decay rate constant (l/t)

First Order Decay Model



Results in BIOCHLOR



Sequential Reactions

$$PCE \xrightarrow{l_1} TCE \xrightarrow{l_2} DCE \xrightarrow{l_3} VC \xrightarrow{l_4} ETH$$

$$Rate_{PCE} = - l_1 C_{PCE}$$

$$Rate_{TCE} = l_1 y_1 C_{PCE} - l_2 C_{TCE}$$

where $y_1 = \dfrac{MW_{TCE}}{MW_{PCE}}$

Sequential Reactions

$$PCE \xrightarrow{l_1} TCE \xrightarrow{l_2} DCE \xrightarrow{l_3} VC \xrightarrow{l_4} ETH$$

$$Rate_{PCE} = -\,l_1\, C_{PCE}$$

$$Rate_{TCE} = l_1\, y_1\, C_{PCE} - l_2\, C_{TCE}$$

Reactive Transport Equations

$$Rate_{PCE} = \frac{d\,C_{PCE}}{d\,t} = L\,(C_{PCE}) - l_1\,C_{PCE}$$

$$Rate_{TCE} = \frac{d\,C_{TCE}}{d\,t} = L\,(C_{TCE}) + l_1\,y_1\,C_{PCE} - l_2\,C_{TCE}$$

$$Rate_{DCE} = \frac{d\,C_{DCE}}{d\,t} = L\,(C_{DCE}) + l_2\,y_2\,C_{TCE} - l_3\,C_{DCE}$$

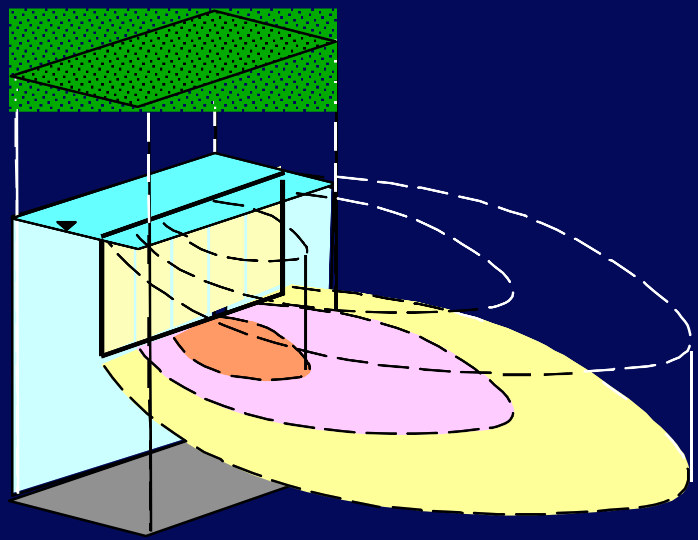
etc. ...

A-D Equation (1-D advection, 3-D dispersion)

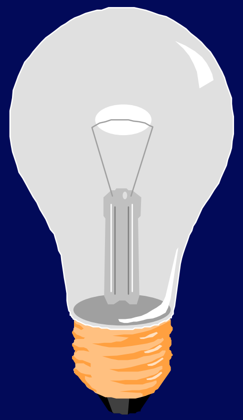
$$L\,(C_1) = -v\,\frac{d\,C_1}{d\,x} + D_x\,\frac{d^2C_1}{d\,x^2} + D_y\,\frac{d^2C_1}{d\,y^2} + D_z\,\frac{d^2C_1}{d\,z^2}$$

BIOCHLOR Model

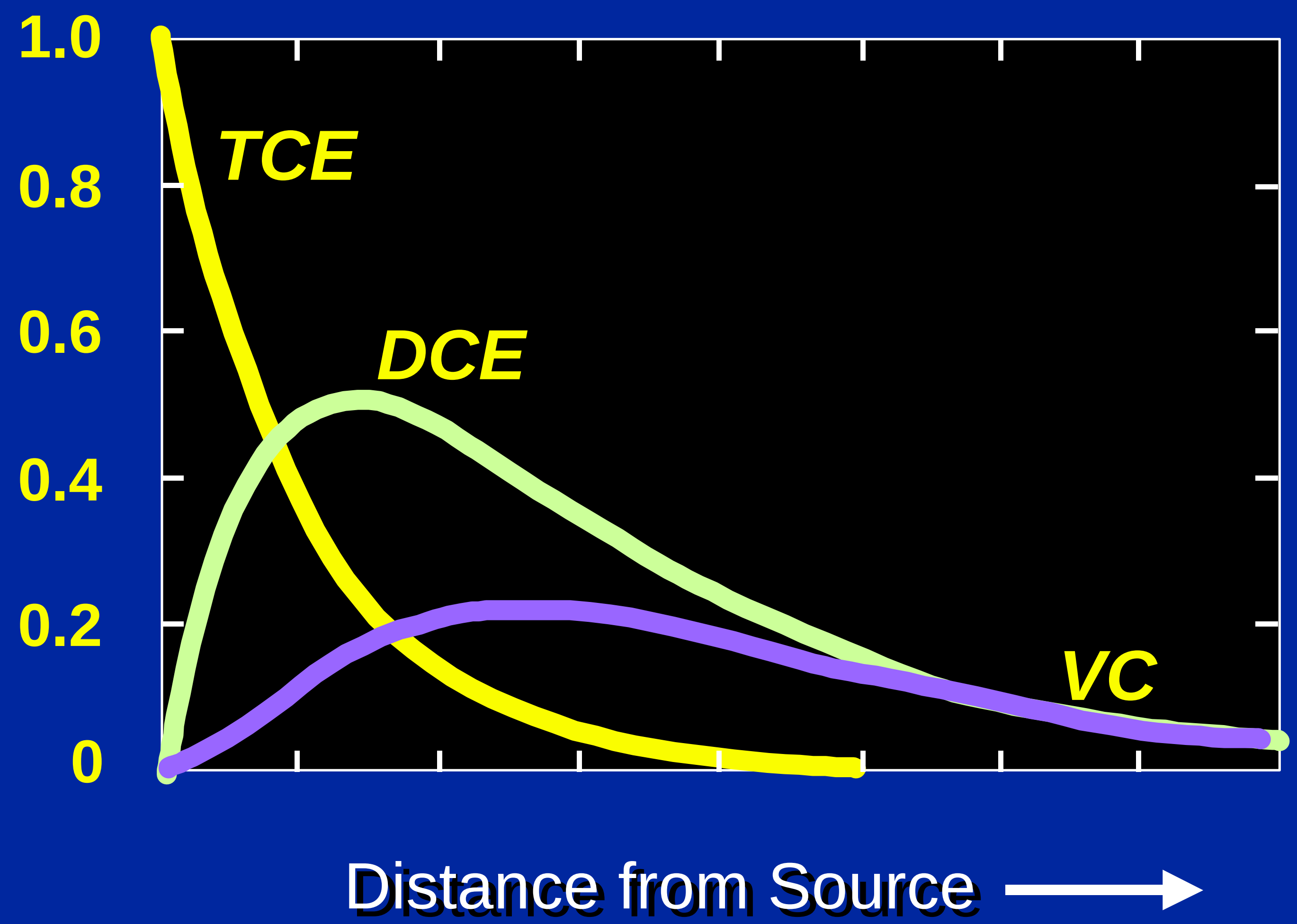
Domenico Solution for Groundwater Transport



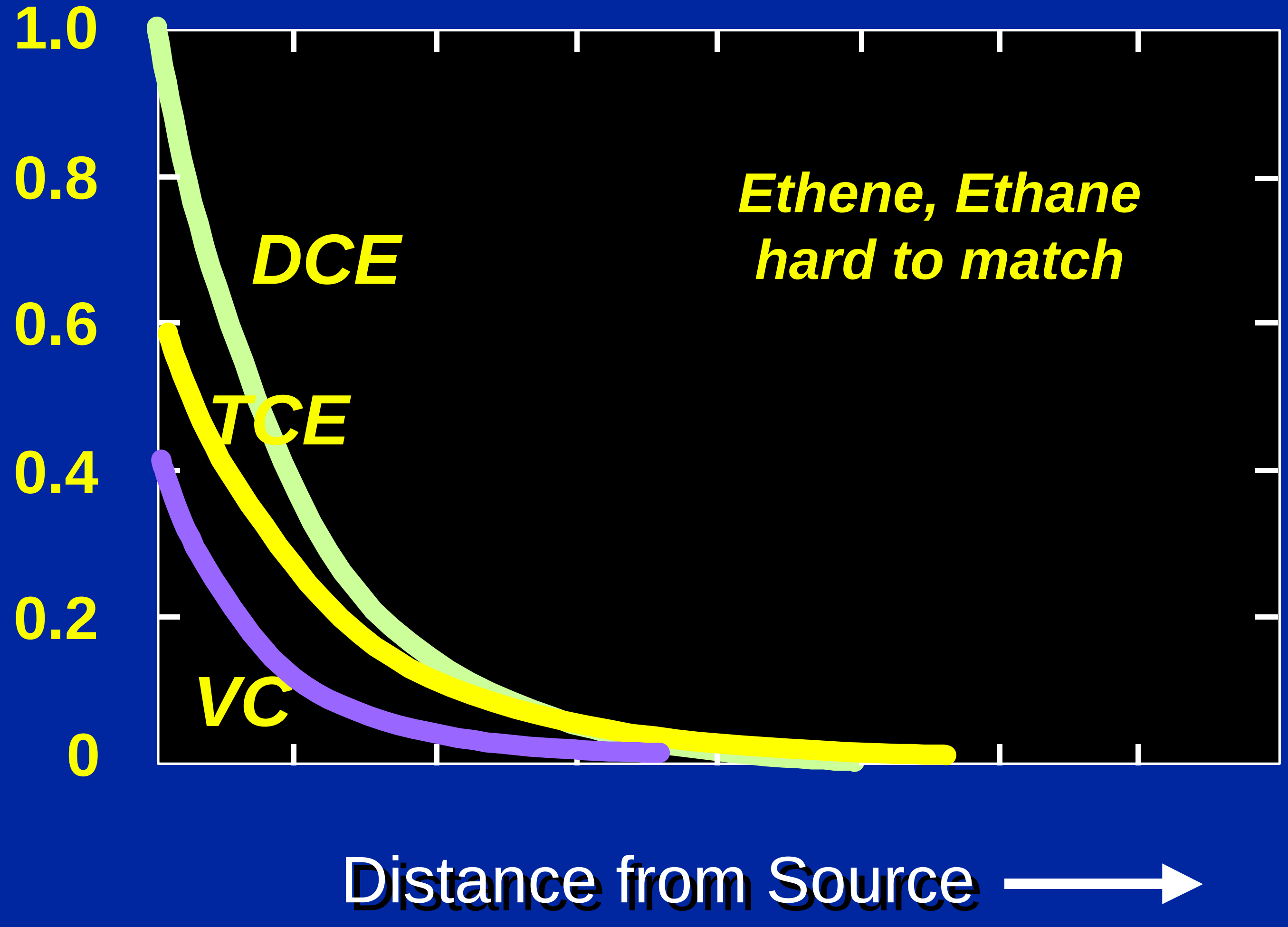
Y. Sun / T.P. Clement Transformation



Results in BIOCHLOR

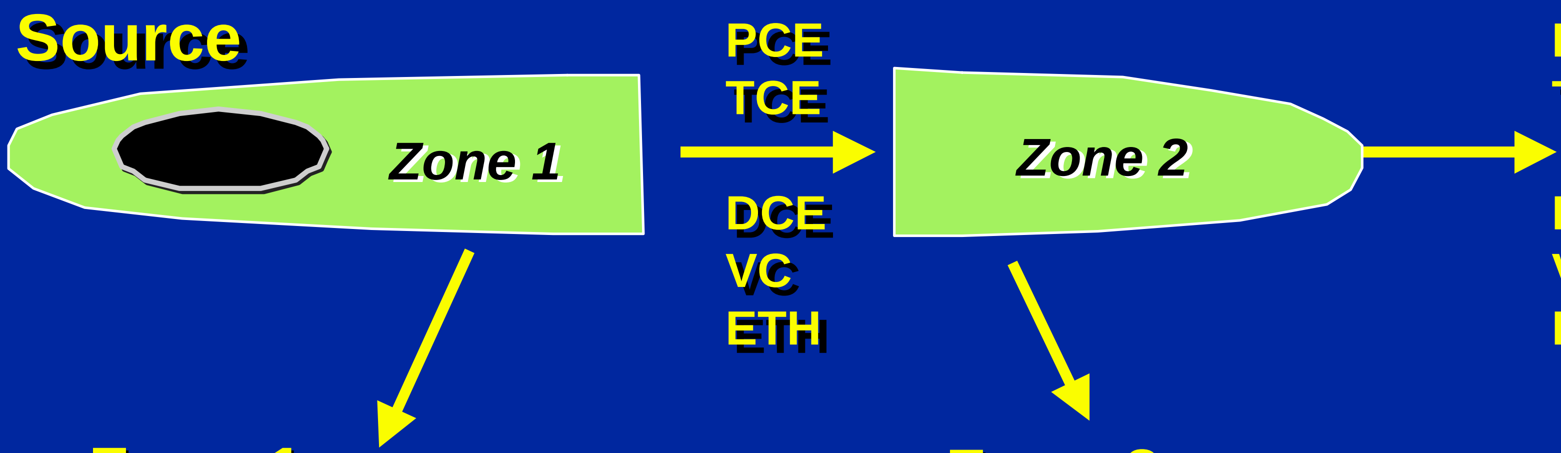


Many Different Types of Solvent Plumes



BIOCHLOR Model: Other Features

Two Reaction Zones for Mixed Sites

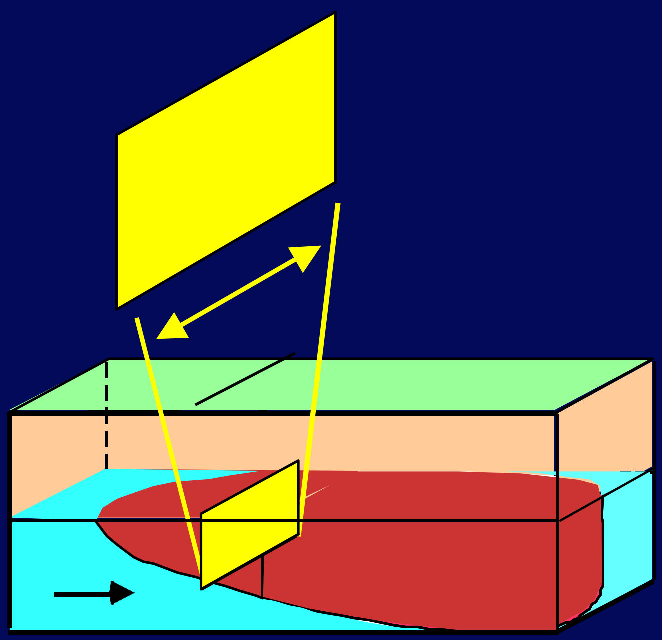


Zone 1:
High Decay Rates
(Carbon Present)
(must be at steady-state!)

Zone 2:
Low Decay Rates
(No Carbon)

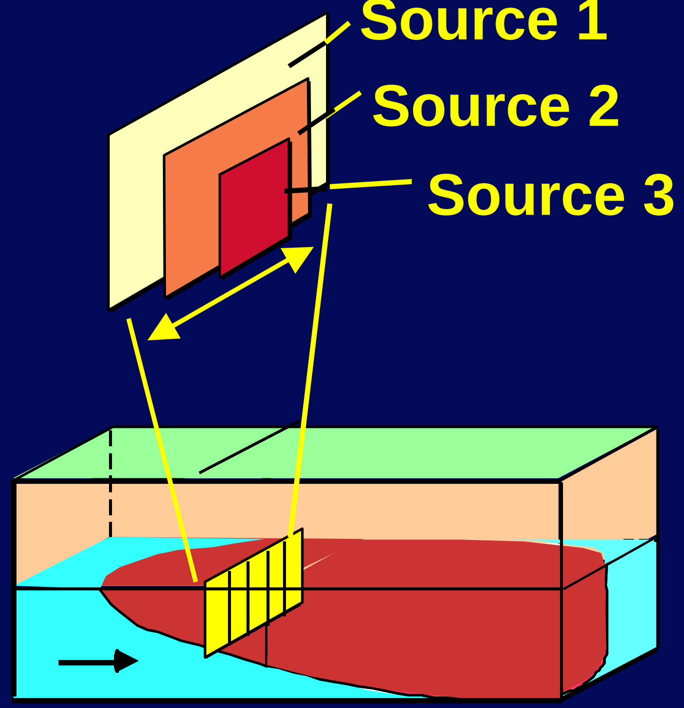
BIOCHLOR Model: Other Features

- **Single Vertical Plane Source**



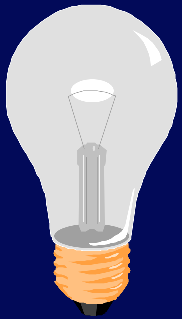
- **Superimposed Sources**

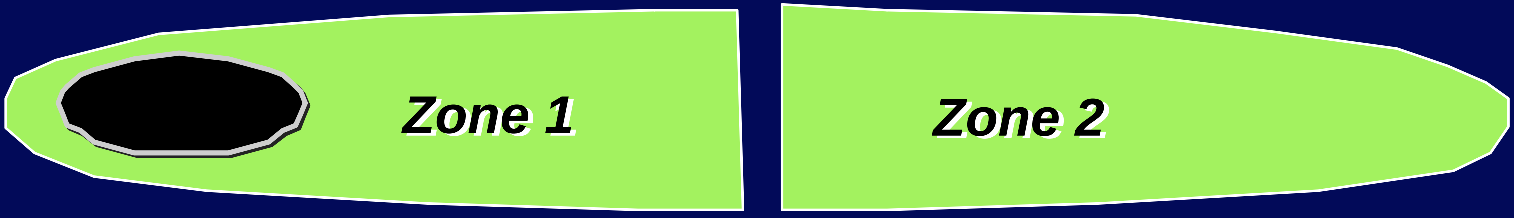
(Connor et al., 1995)



BIOCHLOR Model: Summary

- Predicts Parent, Daughter Compound Concentrations
- Provides Analytical Solution to Transport Equations with Sequential Reactions
- Simulates Two Biodegradation Zones for Mixed Sites

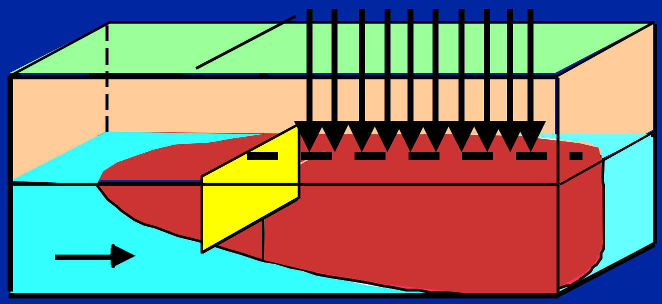




BIOCHLOR
Modeling Tricks

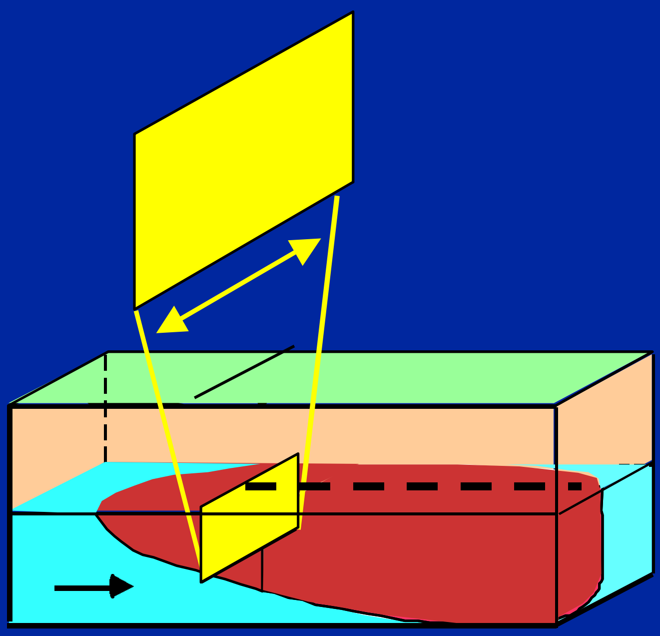
What about changes in mass flux instead of concentration?

BIOCHLOR (and BIOSCREEN) reports mass flux at 10 points downgradient of the source in units of mg/day.

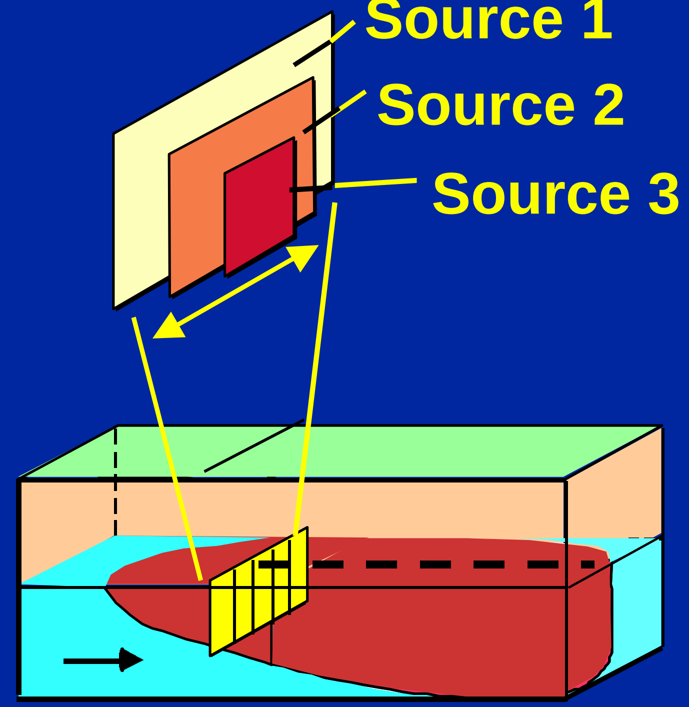


BIOCHLOR
Modeling Tricks

Superimposed source zones not important if you are just looking at centerline concentrations.



OK for many simulations

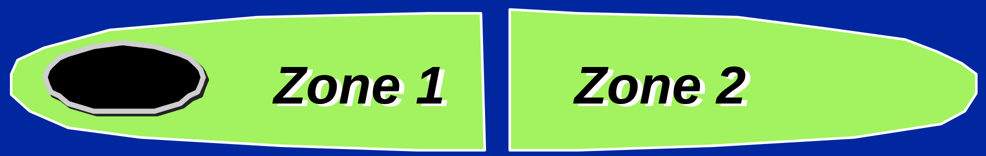


Not needed for centerline predictions

BIOCHLOR
Modeling Tricks

When do you go to two zones?

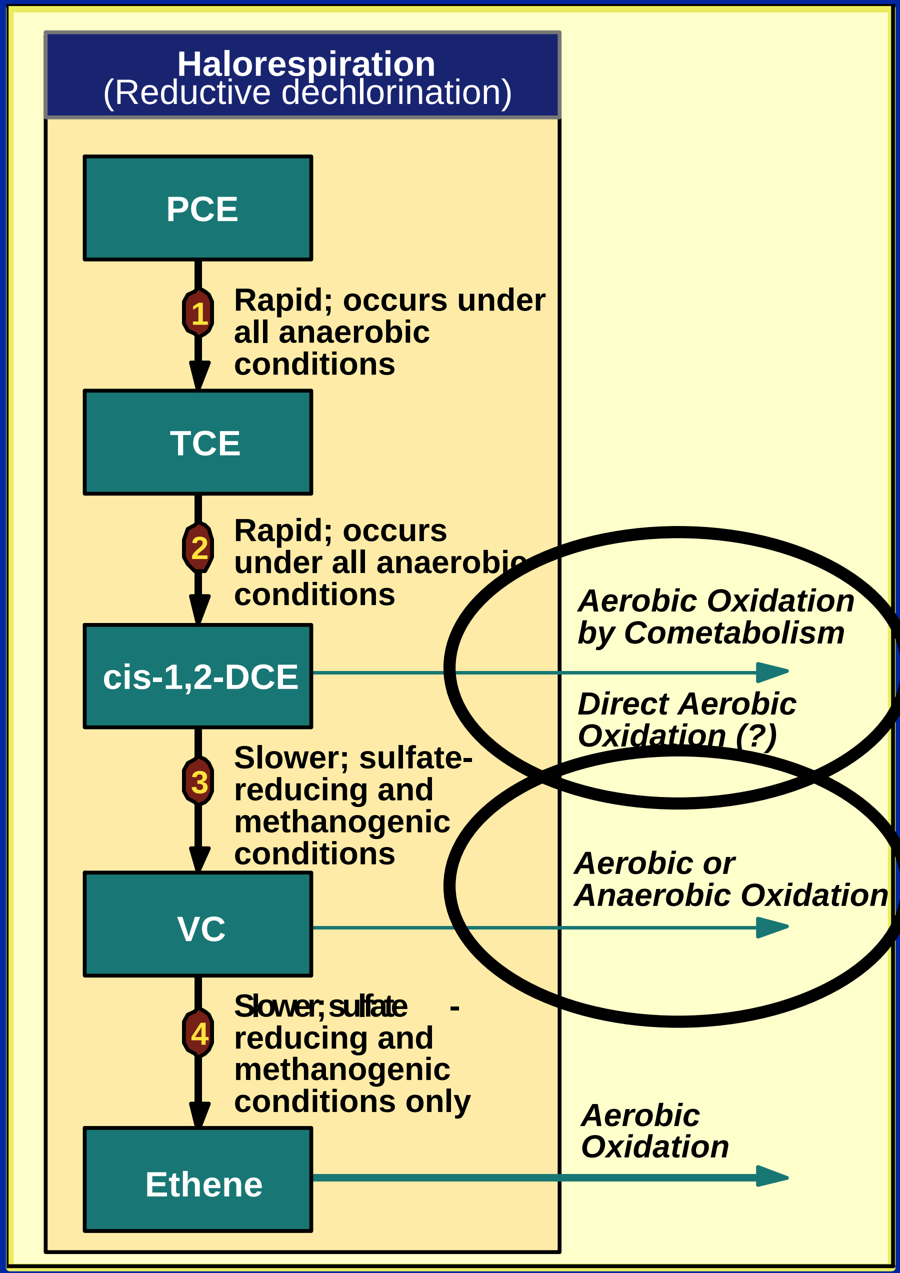
- **Look at DO and methane ratios along centerline of plume**
  - **When DO/methane is high, zone is probably anaerobic.**
  - **When DO/methane gets low, more likely is aerobic.**
- **If ratios change significantly along centerline, two zones may be needed (ease of calibration will confirm this)**



BIOCHLOR
Modeling Tricks

What if not complete reductive dechlorination chain (such as aerobic downgradient in Zone 2)?

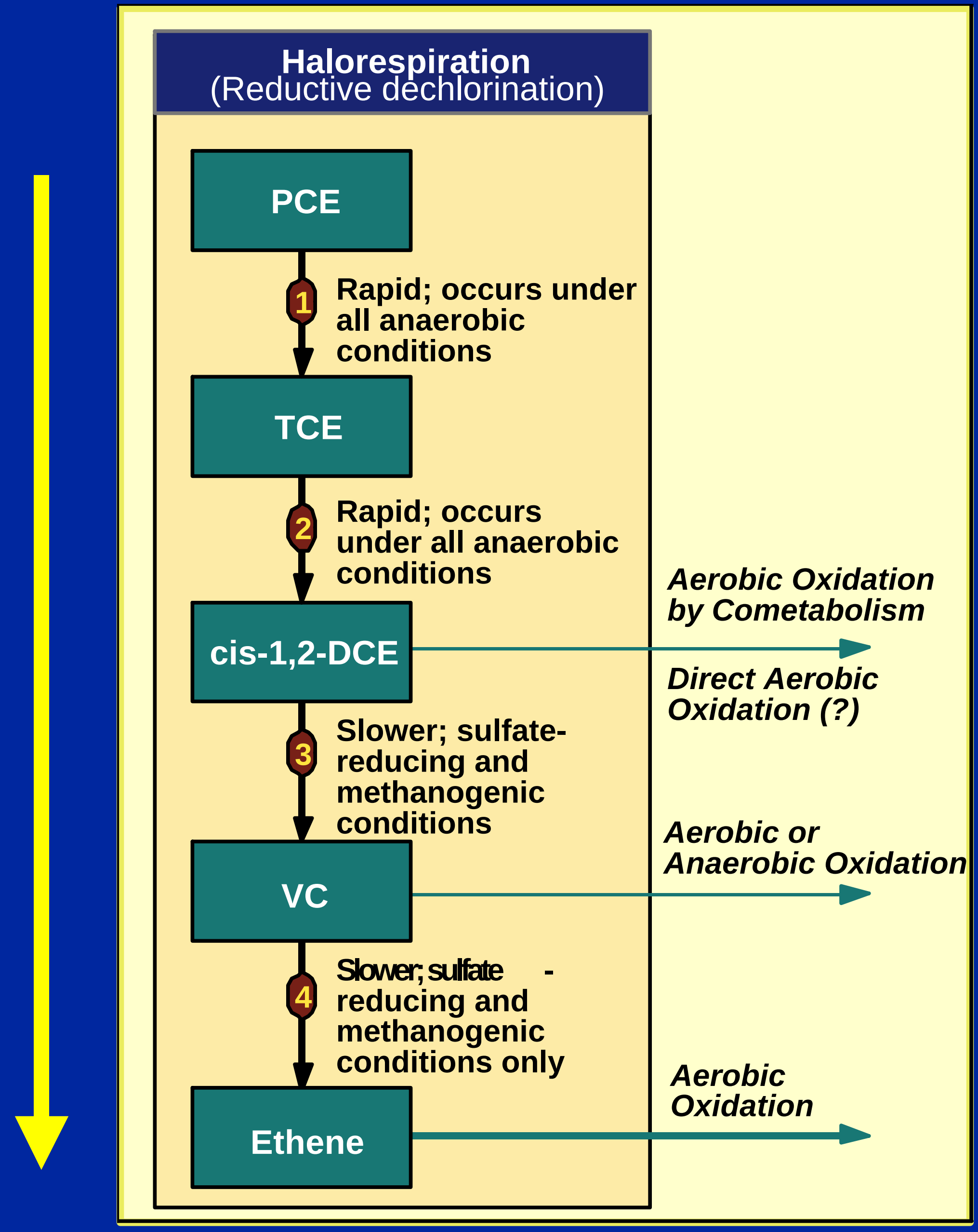
Can use two separate BIOCHLOR runs to get answer for case where cis-DCE and VC are going aerobically in a second zone downgradient of the sourc.



BIOCHLOR
Modeling Tricks

When calibrate, start with parent and work down chain.

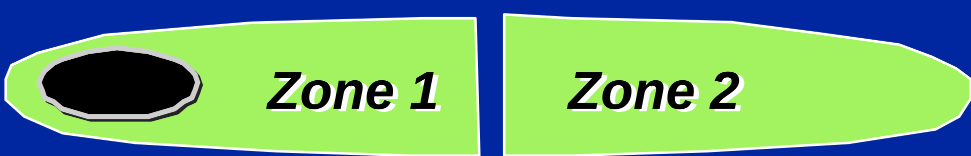
If VC doesn't work out, start again and either add or take out mass from the system by adjusting decay of parents.

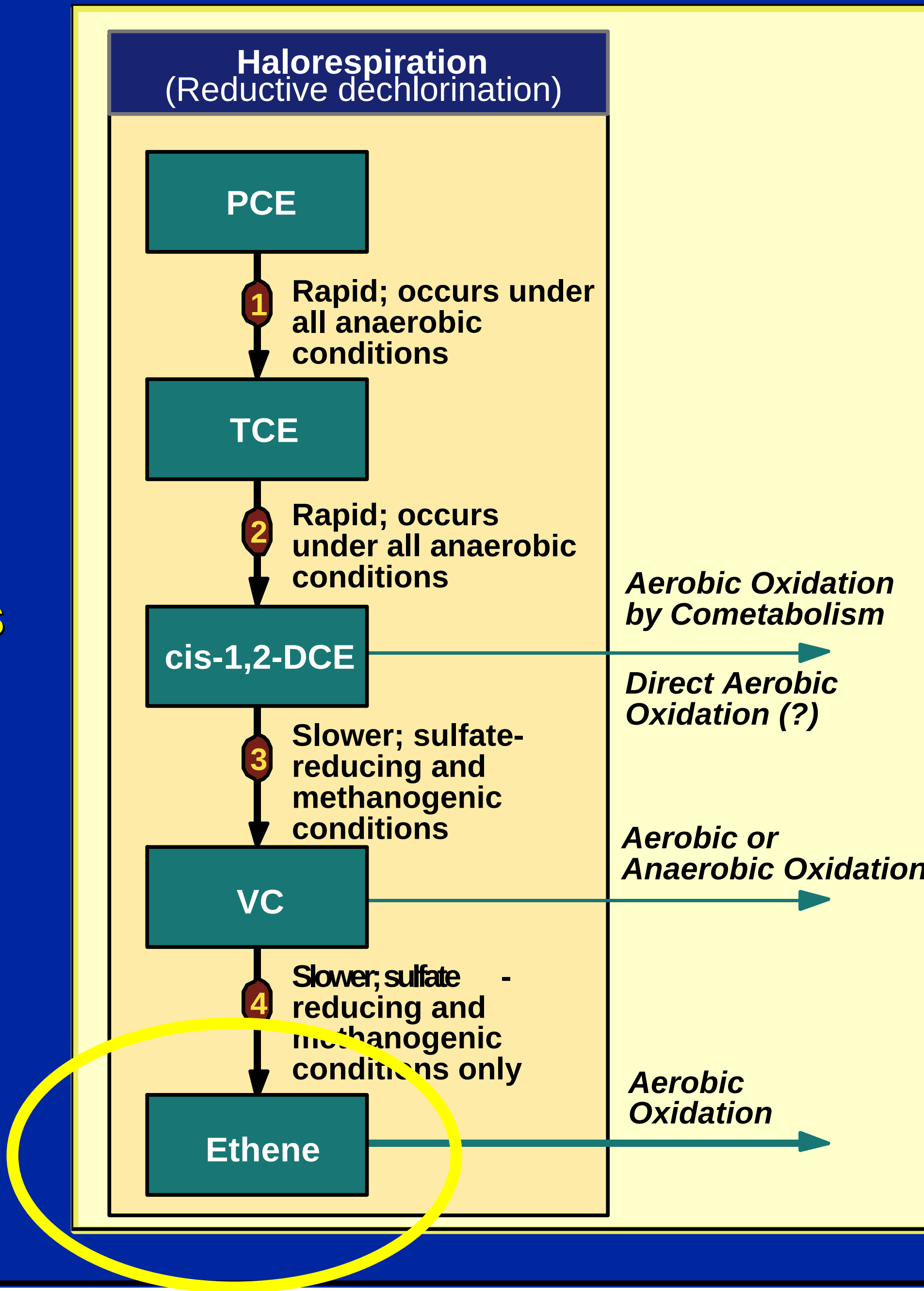


BIOCHLOR
Modeling Tricks

Ethene and ethane are hard to match at sites due to:

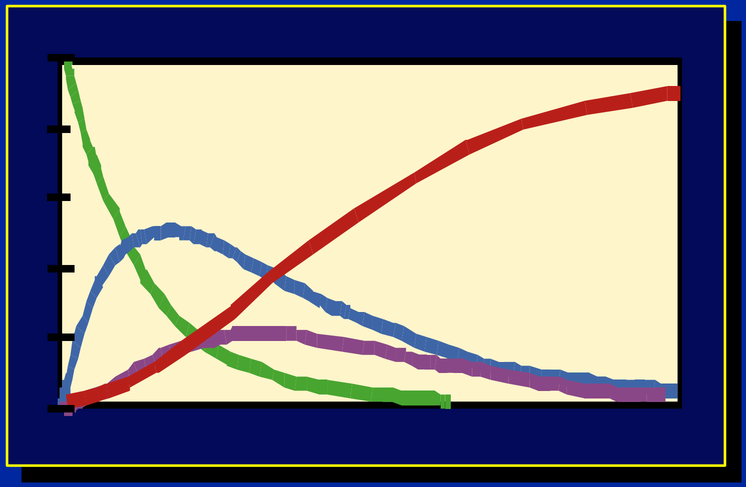
- **degassing of highly volatile gases such as ethene, ethane**
- **biodeg of ethene, ethane**





BIOCHLOR Version 2.0

- Rate Constant Decision Support System
- Source Decay Option
- Animation Feature



How To Get BIOCHLOR . . .

Version 1.0:

- Available on CD *OR*
- Download free

  Currently: www.gsi-net.com

  Jan. 2000: www.epa.gov/ada/models.html
  (CsMOS Web Page)

Version 2.0:

- Available:

  Fall 2000